LUBRICATION AND LUBRICANTS.

A TREATISE ON THE

THEORY AND PRACTICE OF LUBRICATION,

AND ON THE

NATURE, PROPERTIES, AND TESTING

OF LUBRICANTS.

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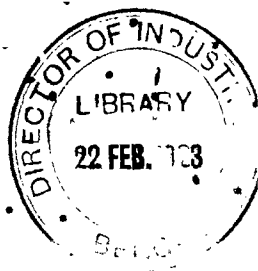
PREFACE TO THE FIRST EDITION.

ALTHOUGH the subject of lubrication and lubricants is by no means unrepresented in our technical literature, we are not acquainted with any one work in which it is adequately treated, in the light of our present knowledge, from the point of view of the engineer and also of the chemist. Nevertheless, it was not without considerable hesitation that we accepted the invitation of the publishers to write a treatise on the subject.

So much still remains to be learned, relating to the chemical constitution and physical properties of lubricants, and also regarding the manner in which they act, under certain circumstances, in reducing friction, that we cannot claim to have produced a complete treatise. We trust, however, that our work, though necessarily incomplete in many respects, will prove of value to the engineer, the chemist, and the manufacturer.

Being the joint production of a chemist and an engineer, the responsibility for the chemical and mechanical sections of the work must necessarily rest mainly upon one or other of the authors; the purely physical sections are, however, to a large extent of joint authorship. Our object has been to, as far as possible, make each section complete in itself. In the first four

chapters, friction, the viscosity of liquids, and lubrication are treated mainly from a theoretical point of view; in the five succeeding chapters, the nature, properties, and testing of lubricants are dealt with; and the two final chapters are devoted to a description and discussion of the practical application of lubricants to machinery for the purpose of reducing friction and wear. In the last chapter, which has been written chiefly for engineers in charge of machinery, many points are again briefly discussed which have already been more fully treated in earlier portions of the work.

The descriptions of oil-testing machines in the chapter on the mechanical testing of lubricants are based almost entirely on published information; but, in the instructions for their manipulation, an endeavour has been made to state the conditions under which tests may be made for "oiliness" or for viscosity, much that has been written on the subject being unsound, owing to a want of knowledge concerning the conditions under which these two properties of lubricants are of active value.

For the theory of viscous lubrication we are indebted, firstly to the experimental work carried out for the Institution of Mechanical Engineers by Mr. Beauchamp Tower, and secondly, to the theoretical explanation of Mr. Tower's results communicated to the Royal Society by Professor Osborne Reynolds, F.R.S. Without losing sight of the valuable work done by other investigators, amongst whom should be mentioned Professors Thurston and Goodman, also Mr. Veitch Wilson, who, as a manufacturer, has laboured for so many years to spread a correct knowledge of the nature and properties of lubricants among users, it is not too much to say that the work done by Mr. Beauchamp Tower and Professor Osborne Reynolds has been mainly instrumental in leading to the adoption of scientific methods of lubrication, and has enabled the part played by the viscosity of the lubricant to be clearly stated. An equally complete treatment of the

theory of oiliness or greasiness is at present impossible; but the bearing upon this important branch of the subject of the investigations on the stability and thickness of liquid films carried out by Professors Reinold and Rücker has been called attention to. Lord Rayleigh's contributions to the theory of superficial forces have also enabled us to show the important part played by superficial tension.

The adoption of more correct ideas concerning the theory of lubrication, and the demand for machines of greater efficiency and power, have led to very rapid improvements in the designs of bearings and in the methods of applying lubricants. Since we undertook to write this work, great progress has been made in this direction. Every endeavour has been made to give the latest practical information, and we trust that, in giving prominence to new designs, we shall not be regarded as having passed over with undue haste older methods and principles which still commend themselves to many practical engineers.

Owing to the advances made during recent years in the manufacture and refining, as well as in the methods of application and testing of lubricants, it is too much to expect that the information which we have sought to convey is, in all respects, up to date. We shall, therefore, gratefully welcome any suggestions on the part of our readers which may enable us in a future edition to remedy defects and supply omissions.

References are given throughout the text to the chief literary sources whence we have derived information. In the case of chemical and physical papers appearing in foreign periodicals, we have referred chiefly to the valuable abstracts published by the Society of Chemical Industry and the Society of Public Analysts. The tables of chemical and physical constants of oils, etc., have been compiled mainly from the data collected by Dr Lewkowitsch for his standard treatise on the analysis of oils, partly from results accumulated in our own experience. *The Engineer* has also been freely quoted.

Our best thanks are due to Mr. C. E. Wolff, B.Sc., for assist-
ance in some of the mathematical portions of the work; to Mr.
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L. ARCHBUTT.
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PREFACE TO THE SECOND EDITION.

WE very much regret the delay which has occurred in the issue of this second edition of our work, but we hope that the thorough revision which the book has undergone, the rearrangement of some of the subject-matter, the addition of nearly seventy-five pages of new matter, and the enlargement and improvement of the index, will atone for the inconvenience caused by the book being out of print for so long a time. We have been much gratified by the favourable reception accorded to the first edition, of which a French translation has been issued; and the numerous inquiries for the second edition which we have received prove that the book has met a want.

The volume has been revised throughout, but the chief additions have been made to the last three chapters.

In Chapter IV. a brief account of Lasche's experiments on the friction and lubrication of motor bearings at high speeds is given. Doolittle's Torsion Viscometer is described in Chapter VI., and some errors in the table for converting hydrometer degrees into specific gravities have been corrected. In Chapter IX. a full description will be found of Thurston's Oil-testing Machine as modified by us, together with a description of the method of using the machine which we have found most advantageous, and the results of a number of tests which

we have made. Experience has taught us that to obtain results of value from this machine, and doubtless also from others of similar type, much patience and careful observation are required. Descriptions will also be found in this chapter of several machines which were not included in the first edition, or which have been more recently designed; also an account of Professor Kingsbury's experiments on the friction of screws.

The subject of bronze bearings and anti-friction alloys has been treated at length in Chapter X., and an account is given of the most important researches. The tables giving the composition of these alloys have been entirely re-written, and the authorities added. Where no authority is mentioned, the composition stated is mostly based upon our own analyses. Fresh measurements of the thickness of lubricating films by Professor Kingsbury are given on p. 397. Our best thanks are due to Mr. H. Fowler for kindly revising the pages on ball and roller bearings. The descriptions of modern methods of lubrication and lubricators have been largely added to, and we have pleasure in acknowledging our indebtedness to several firms whose names are mentioned in the text, for the loan of blocks.

In the last chapter, under the heading "Lubrication of Miscellaneous Machines," we have given particulars of the oils which are suitable for the lubrication of the principal types of machinery and engines, and we trust this information will prove useful. Mr. J. Veitch Wilson and other experts whom we have consulted have been kind enough to give us the benefit of their experience in regard to many machines which are outside the range of our own special experience. To these gentlemen, and to Sir Boverton Redwood who has kindly revised the pages on Mineral Oils in Chapter V., we tender our acknowledgments and sincere thanks. We also wish to thank the American Society of Mechanical Engineers, the Pennsylvania Railroad Company, and the Proprietors of *Engineering* for permission

to quote from their publications; also Dr. Henry Leffmann, Mr. H. F. Moore, Professor Goodman, and several other correspondents and friends whose names are mentioned in the text, for suggestions and information very kindly communicated.

L. ARCHBUTT.
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CONTENTS.

CHAPTER I.

FRICTION OF SOLIDS.

CHAPTER II.

INTERNAL FRICTION, OR VISCOSITY, OF LIQUIDS.
PLASTIC FRICTION.

CHAPTER III.

SUPERFICIAL TENSION.

CHAPTER IV.

THE THEORY OF LUBRICATION.

CHAPTER V.

LUBRICANTS—THEIR SOURCES, PREPARATION, AND
CHIEF PROPERTIES.

CHAPTER VI.

PHYSICAL PROPERTIES AND METHODS OF EXAMINATION OF LUBRICANTS.

CHAPTER VII.

CHEMICAL PROPERTIES AND METHODS OF EXAMINA-
TION OF LUBRICANTS

xii

CONTENTS.

CHAPTER IX.

THE MECHANICAL TESTING OF LUBRICANTS.

CHAPTER X.

THE DESIGN AND LUBRICATION OF BEARINGS
AND OTHER FRICTION SURFACES.

CHAPTER XI.

THE LUBRICATION OF MACHINERY.

LIST OF TABLES.

MEANING OF THE SYMBOLS EMPLOYED
IN THIS WORK.

A - Area.

a and l.—Dimension in the direction of motion.

b.—Dimension at right angles to direction of motion.

c.—A constant.

F.—Total resistance.

f.—Resistance per unit of area.

g.—Acceleration due to gravity.

H.—Unit of heat.

h.—Head of liquid.

k.—A constant.

N.—Revolutions per minute.

P.—Total pressure.

p.—Pressure on unit area.

T.—Force of tension or compression.

r.—Radius or distance from a centre line.

r_o.—Radius of a tube or cylinder, or half the distance separating two planes.

t.—Time.

V.—Volume.

v.—Velocity.

v_1.—Maximum velocity.

$\bar{v}$.—Mean velocity.

W. and w.—Weight or load.

η.—Viscosity.

μ.—Static coefficient of friction.

μ_1.—Kinetic coefficient of friction.

π.—Ratio of circumference to radius.

τ.—Thickness.

d.—Relative density.

σ.—Value analogous to density.

LUBRICATION AND LUBRICANTS.

CHAPTER I.

FRICTION OF SOLIDS.

Introductory.—The object of mechanism of all kinds is the control or utilization of energy for the purpose of doing useful work. Owing, however, to the necessary imperfections of our methods, a large part of the energy applied is wasted in various ways; mainly, in overcoming the resistance to relative motion offered by the opposing surfaces of the machines themselves.

The least force properly applied to a perfect machine at rest should set it in motion, and, owing to the inertia of its parts, such a machine once set in motion, but not doing work, should continue to move with uniform velocity; but there are causes which operate to arrest motion, firstly, the inertia and frictional resistance of the air; secondly, the friction between the rubbing surfaces of the machine; and thirdly, induced electrical currents. The frictional resistance of the air may be reduced by shaping the moving surfaces of the machine so as to oppose the least surface to its action; with the electrical resistances we are not here concerned. The most serious resistance to the motion of heavy machinery is the friction between the opposing surfaces, and it is in order to reduce this friction to a minimum that lubrication is resorted to.

In some cases the frictional resistance between opposing surfaces is utilized as a means of transmitting motion from one portion of a machine to another, or from machine to machine. Friction clutches and belt, or rope gearing may be instanced as cases in point. Here the object is to make the frictional resistance as great as possible, so that the opposing surfaces may not slip. Such devices are, however, beyond the scope of this work, for, although friction surfaces are often lubricated to a certain extent, the lubricant is applied to prevent the surfaces from seizing, and not to reduce friction. There are also instances in which lubrication is resorted to chiefly in order to

reduce the wear of the friction surfaces, and this may be of such importance that the loss of energy by friction becomes quite a secondary consideration.

Lubrication is effected by interposing between the friction surfaces films of liquid or soft solid substances which decrease the friction. Such substances are called lubricants. The physical properties upon which their lubricating powers depend will be considered at a later stage; for the present we shall confine our remarks to a discussion of the nature and laws of so-called solid friction, *i.e.* the friction between clean solid surfaces. Such surfaces are seldom chemically clean; but the contaminating films do not affect the laws of solid friction, they only determine the degree of resistance.

Friction is not merely a resistance to the relative motion of solid surfaces. The changes of shape undergone by solids when under stress, as well as the movements of liquids, are opposed by internal friction, which, in these cases, is of quite a different nature and obeys different laws to the friction between opposed surfaces. Other chapters will, therefore, be devoted to the consideration of liquid friction, whilst in the present one the phenomena presented by the friction between solid surfaces only will be discussed.

Nature of Friction.—When two solid surfaces are pressed firmly together, they cannot be moved relatively to each other without the exercise of considerable force; and when, by a sufficient effort, the surfaces have commenced sliding against each other, the resistance to be overcome in order to keep them in relative motion, though it may be either greater or less than was required to start them from a state of rest, has at all speeds a considerable retarding effect, and is called the friction between the surfaces. The frictional resistance varies greatly between different surfaces and materials, being least between hard and polished, and greatest between soft and rough surfaces. Between leather and coarse sandstone, for example, its value is very considerable, and it is owing to this fact that we are enabled to stand and walk in such perfect security on ordinary ground. Between leather and ice there is very much less friction. Walking on ice is, consequently, less secure than walking on the ground, and progression is more safely and easily effected by skating or sliding.

In the sliding or rolling of solids against each other, friction owes its existence almost entirely to the roughness or unevenness of the surfaces in contact. Even apparently smooth surfaces are not free from minute elevations and depressions which interlock when such surfaces are pressed together. Motion can then only result either by the passage of one set of inequalities over the other, or by the forcible breaking off of projecting parts. When this takes place, the surfaces may be continuously abraded, for it does not follow that they will be rubbed smooth by the friction.

Friction between surfaces of unequal hardness results in the more or less rapid abrasion of the softer surface, the harder surface suffering very slightly, unless particles removed from it, or derived from

extraneous sources, become embedded in the softer surface and act as graving tools. This is what occurs in the process known to mechanics as 'lapping,' in which emery or some other very hard substance is pressed into the surface of a soft metal, such as lead, which merely acts as a holder for the cutting material.

Friction may be greatly diminished by making the contact surfaces very smooth, and of exceedingly hard materials. Absolutely smooth surfaces cannot be produced, even the most perfectly polished surfaces being more or less uneven.

Rolling friction is of much the same nature as sliding friction. Upon perfectly plane surfaces the friction of rolling would be *nil*, but, as has just been pointed out, such surfaces cannot be produced, and inequalities remain which interlock and form obstacles to free motion. Moreover, pressure causes more or less deformation, both of the plane surface and of the face of the roller, so that contact takes place, not upon a line, but upon a more or less broad strip, and as the roller moves along, fresh portions of the surfaces become distorted and some sliding friction occurs. Nevertheless, for the same load, much less resistance is offered to motion by rolling friction than by sliding friction. A block of stone which would require the exertion of great force to push or drag it over the ground, can be moved with comparative ease upon wooden rollers. Vehicles are, for the same reason, provided with wheels; and, of late years, the substitution of rolling for sliding friction has been extensively applied in the roller and ball bearings of electro-motors, tram-cars, cycles, churns, clocks, astronomical telescopes, and many other machines and instruments where the pressure upon the surfaces is comparatively light. With this kind of friction, substances such as indiarubber, in the form of wheel tyres, for example, may be used to roll over comparatively rough surfaces without much loss of energy, the elasticity of the one surface enabling it to change its form to suit the inequalities of the ground.

Circumstances which Influence Friction.—*Cohesion.*—A cause of friction remains to be considered which is aggravated rather than diminished by our efforts to produce smooth surfaces. The more perfect the surfaces, the more closely will they be brought into contact, and at very small distances molecular forces come into play which cause very true surfaces to adhere strongly and thereby resist sliding impulses. Two pieces of plate-glass, for instance, carefully cleaned from dust, may, if placed upon one another and pressed together with a sliding motion, be caused to adhere [1] so strongly that one may be lifted and even held in a vertical position by means of a handle of sealing-wax attached to the other; indeed, a skilled workman can render the surfaces so nearly true that they cannot again be separated without breaking the glass, the points of contact having become practically *welded* together. In like manner pieces of marble,

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[1] A distinction is sometimes drawn between 'adhesion' and 'cohesion' which is not warranted by the facts. See Tait; *Properties of Matter*, 3rd edition, p. 241.

upon which true surfaces have been worked with great care, adhere when pressed together, and even *in vacuo* their cohesion may be so great that comparatively large masses may remain suspended in virtue of their mutual molecular attractions. Clean, true surfaces of copper adhere when pressed together; and Barton, early in the last century, showed that a dozen small cubes of this metal, whose sides he had made very true, when piled one on another adhered when the upper one was lifted. Whitworth showed, more recently, that other substances may be caused to exhibit similar attractive forces.

In such instances as have been adduced, the materials may generally be parted again without injury; but two surfaces of lead which have been freshly scraped, if pressed together with a screwing motion, will adhere almost as firmly as if they formed one mass. In other words, such surfaces when rubbed together 'seize,' *i.e.* the materials composing them undergo a process of cold welding. Prof. Walthère Spring has shown that the dust of most metals, if subjected to sufficient pressure, may be made to unite into solid blocks, and even alloys of two or more different metals may be thus produced.[1] The pressure required is very much greater with a hard metal, such as aluminium, than with a soft metal like lead, but all the metals experimented upon were found to weld at ordinary temperatures, if sufficiently compressed. Of course, the pressures used in these experiments were far greater than are brought to bear upon ordinary bearings; but, as shown above, cohesion commences between very smooth surfaces under very moderate pressures, and the increased friction thus set up rapidly causes the bearings to become heated. This reduces the pressure at which welding takes place, and as soon as the welding pressure coincides with that to which the bearing is subjected, the metallic surfaces seize or abrade each other.

Spring has, in fact, shown more recently[2] that by raising metals to temperatures far below their melting points, welding can be caused to gradually take place under quite moderate pressures, and that even alloys of dissimilar metals can be formed in this way. The metals experimented upon were turned into cylinders, with ends as perfectly plane as possible, and these were firmly pressed together by means of a screw. After heating for several hours at $200° - 400°$ C., the cylinders of most similar metals became so firmly welded together that, if broken in a vice, the fracture did not take place along the original surface of separation. Dissimilar metals, treated in the same way, became alloyed at the junction.

In these experiments, the welding and alloying effects were caused by the surface molecules actually diffusing into each other. The late Sir William C. Roberts-Austen, who published several investigations on the rate of diffusion of metals into each other, wrote, in 1897[3] "The continuation of the experiments has led to the recognition of

[1] *Bull. Acad. Belg.*, 1880 (2), xlix., 323.
[2] *Zeit. physikal. Chem.*, 1894, xv., 65.
[3] *Fourth Report to the Alloys Research Committee*, p. 58.

the remarkable fact that diffusion of metals can readily be measured not only in molten but in solid metals. It is certainly remarkable that gold—placed at the bottom of a cylinder of lead 3 inches high, and heated to only 200° C. or 400° F., which is far below its melting point, and while it is to all appearance solid—will have diffused to the top in notable quantities by the end of three days. . . . The experiments summarized have already led to the recognition of the undoubted fact that it is possible actually to observe and measure the migration of the constituent atoms in a metal or alloy at the ordinary temperature."

Surface Contamination.—All exposed surfaces are liable to undergo change, owing to the chemical action of gases and vapours contained in the atmosphere, and to other causes; and the films of oxide, sulphide, grease, oil, dust, dirt, etc., produced in this way modify the effects of cohesion. Thus, in the experiment with lead described above, unless the metallic surfaces are perfectly bright and untarnished, though they will cohere strongly, they will not weld in the cold. Contamination films, however, except when the pressures are small and the rate of motion slow, are soon rubbed out. Under all circumstances, therefore, where the heat due to friction can accumulate, that is, where it is not produced so slowly or in such small amount as to be conducted away as rapidly as formed, a solid or fluid lubricant must be interposed between the adjacent surfaces, if only to keep them sufficiently apart to prevent friction due to cohesion.

Although the chemically clean and true surfaces of such metals as lead, tin, or wrought-iron will not slide upon each other without seizing, cast-iron may with impunity move in contact with wrought-iron and steel, even when the surfaces are clean and the pressures moderately great; indeed, dissimilar metals always work better and with greater ease upon each other than do similar ones. The foregoing statement may seem to conflict with results which I have been obtained in measuring the frictional resistance between similar metals. In every case, however, when this has been done between 'tough' metals, there is reason to suppose that the surfaces were not chemically clean; for, although experiments have been made both with and without lubricants, in most cases the condition of the unlubricated surfaces has been described as 'unctuous.'

The friction between most so-called 'unlubricated' metallic surfaces is, therefore, not a case of true friction between pure metals, but between surfaces contaminated by atmospheric agencies, by grease, etc., derived from the material with which the surfaces were wiped, or by chemically formed films, such as oxides, sulphides, etc.; in other words, the surfaces are *partially lubricated*. Under moderate pressures such films prevent the actual adhesion of metal to metal, if the rate of motion be not too high and the action not too prolonged. This must be clearly borne in mind, otherwise what is known as 'solid friction' will not appear in its true light. However, so far as is at present known, the laws of friction between contaminated sur-

faces, and such clean surfaces *as will run together*, are identical. A "contaminated surface" is not to be regarded as one that is necessarily defiled, but merely one that has foreign matter on it.

The following experiment will illustrate the effect of a slight contamination film upon a metallic surface:—

A smooth file passed over the freshly prepared, clean surface, will be found to cut well, even when gently pressed against the metal, but if the hand be passed over the metallic surface, the film of grease thereby deposited will so lubricate it that considerably greater pressure on the file is now needed to cause it to cut. If it were not for the presence of this contamination film, soft or tough metals, such as tin, wrought-iron, brass, etc., would at once seize if rubbed together, even at low speeds. Even with moderate loads, inequalities of the surfaces may project through the film and largely increase the frictional resistances. Until this takes place, the value of the friction-coefficient seems to depend as much upon the smoothness of the surfaces and the nature of the foreign substances interposed as it does upon the nature of the materials in contact.

Coefficient of Friction.—The relationship borne by the *frictional resistance* to the *load or force* pressing the surfaces together has been the subject of much speculation and discussion, and although numerous experimental researches have been carried out, such as those of Amontons, Coulomb, Vince, Rennie, Morin, Kimball, and others, there has always been much conflict of opinion. From what has been stated concerning the action which solid surfaces in close contact have upon each other, it will be clear that, although it may be possible to formulate somewhat general laws of solid friction, such laws cannot be expected to hold good under extremes of pressure or speed; and they will be affected to some extent by the nature of the materials in contact and the surface conditions.

The apparatus used by Morin for measuring the friction between surfaces consisted of a loaded box or slider, resting on a horizontal slide. A cord, fastened to the slider, passed over a pulley and carried a smaller suspended box, which could be loaded with any desired weight. Both slider and slide could, after each set of experiments, be replaced by others of different material. By placing weights in the suspended box (the slider being loaded) force was applied in a direction *parallel* to the sliding surfaces, and when the slider began to move, the weight of the small box was a measure of the frictional resistance.

In a particular experiment, the weight of the slider being one ton (2240 lbs.), a force of 350 lbs. was required to cause it to move.

Then, $$\frac{350}{2240} = 0\cdot156 = \mu_1$$

which is called the *coefficient of friction*, while

$$350 \text{ lbs.} = F$$

is known as the *total frictional resistance*.

FRICTION OF SOLIDS.

The coefficient of friction may be defined as that value which, when multiplied by the pressure normal to the surfaces in contact, gives the measure of the maximum frictional resistance to motion.

Making W the weight normal to the surfaces :—

$$\frac{\text{Frictional resistance}}{\text{Normal weight}} = \frac{F}{W} = \mu_1 = \text{Coefficient of friction.}$$

Static and Kinetic Coefficients.—In some cases it has been found that the force F required to keep a body in motion differs from that required to move it from a state of rest. Obviously there must be two coefficients of friction, of which the static (μ) may differ from the kinetic (μ_1). As a rule the kinetic coefficient, or coefficient of friction of motion, is alone of importance in machine work, for owing to the freedom or elasticity of the moving parts, or the vibrations generated at starting, the static coefficient does not make itself seriously felt. Hence the term "coefficient of friction" means coefficient of kinetic friction," unless otherwise stated.

The excess of the static coefficient over the kinetic is most marked in the case of substances such as timber, whose surfaces may be sensibly *indented* by pressure. When such surfaces have remain d for some time in contact under pressure, and at rest relatively to each other, considerable force steadily applied is required to cause them to slide. A similar effect on the resistance to motion is shown in the process of starting a heavy goods train. With all the couplings tight, and the train at rest, the engine is unable to set the wagons in motion. The driver, therefore, reverses his engine until a sufficient proportion of the buffers are in contact and the couplings slack ; he is then enabled to set the wagons in motion one at a time, and so deal with the static or low-speed friction in detail.

Solid Friction—*Rennie's Experiments.*—Rennie[1] made a number of experiments on the coefficient of friction between certain metals at moderate speeds. From the smallness of the coefficient of friction with light loads it would appear that he experimented with contaminated surfaces. The following table gives some of the results he obtained :—

TABLE I.—COEFFICIENTS OF FRICTION BETWEEN METAL SURFACES.

	Brass.	Steel.	Cast-iron.	Wrought-iron.	Tin.
Brass, . . .	·175	·139	·141	·135	...
Steel, . . .	·139	·146	·151	·181	...
Cast-iron, . .	·141	·151	·163	·170	·179
Wrought-iron, .	·125	·181	·170	·160	·181
Tin	...	...	·179	·181	·265

Brass upon other metals gave the least frictional resistance, and tin upon other metals the highest average resistance. Tin upon tin and brass upon brass both gave high figures—they were evidently, even under small loads, showing signs of incipient seizing, owing to the rupture of the interposed film at numerous points. These coefficients

[1] *Phil. Trans.*, 1829, p. 143.

are, however, much greater than those given by certain antifriction alloys when working upon iron or steel. R. H. Smith, who has submitted the alloy known as 'Magnolia metal'[1] to a variety of tests, gives the following figures, the bearing running dry :—

Nominal pressure lbs. per sq. in.	Speed in feet per min.	Coefficient of Friction μ_i.
99·5	52·3	·0713
99·5	62·7	·0663
99·5	78·4	·0618

Owing to the low friction-coefficient of this alloy, a bearing may be run dry at considerable speed without serious injury resulting. The alloy also answers well for bearings which have to carry moderately heavy loads and run at moderate speeds, or which, owing to their positions, can only be supplied with water.

Friction and Speed.—In all cases, the static coefficient is sensibly the same as the low-speed kinetic coefficient with imperfectly lubricated metallic surfaces, such as might be used for bearings; but between oak and oak and other soft materials, the kinetic friction at the speeds used in practice is considerably less than the static friction. Jenkin and Ewing[2] found, however, that the change in the value of the friction-coefficient is not abrupt. In fact, it is highly probable that in the cases where the static coefficient differs from the kinetic, the latter gradually changes when the velocity becomes extremely small, so as to pass without discontinuity into the former.

From a number of experiments made by Kimball[3] it would also appear that, although there is no abrupt transition between the static and kinetic coefficients, the friction of motion is not always less than the friction of rest. This is more particularly the case when the loads are small or the surfaces are lubricated.

With clean or nearly clean surfaces, and light loads, Kimball found that the kinetic coefficient of friction at very slow speeds was greater than the static coefficient, but that with increasing speed the coefficient reached a maximum and then decreased. This he illustrated by an experiment which measured the friction of a leather belt hung over a cast-iron pulley. To one end of the belt a known tension was applied by means of a fixed weight; to the other end a spring dynamometer was attached. The tension of the ends of the belt being known, the coefficient of friction was easily found. In the following table the coefficients given are relative only :—

TABLE II.—RELATIVE COEFFICIENTS.

Feet per Minute.	Relative Coefficients.	Feet per Minute.	Relative Coefficients.
18	·82	1190	·96
92	·93	1980	·82
660	1·00	1969	·69

[1] See Table, p. 389.   [2] *Proc. Roy. Soc.*, 1878, p. 509.
[3] *American Journal of Science*, 1877, p. 353.

Kimball considered that the results he obtained reconcile the apparently conflicting statements of Morin, Boshin, Hirn, Coulomb, and others, for these investigators experimented under very different conditions of velocity, pressure, etc.

Morin experimented under conditions which gave him a coefficient approaching the maximum, and thus his results were approximately constant for all the speeds tried. Bochin experimented with railway trains; his conditions were high speeds, hard contact surfaces, and great intensity of pressure. These circumstances, under some conditions of lubrication, favour a coefficient *decreasing* as the velocity increases. Hirn, on the other hand, employed very light pressures, less than two pounds on the square inch, and kept his contact surfaces so thoroughly lubricated that the friction was rather between oil and oil than between two metallic surfaces. These conditions, at ordinary speeds, favour a coefficient *increasing* as the velocity increases. For the effects of speed to be ascertained, either the metals in contact must be such that they will not seize as they become heated, or one or both of the contact surfaces must be continually changing. Both these conditions are fulfilled by railway brakes. When the wheel is revolving and rubbing against the brake block, the contamination of both surfaces is practically rubbed away, and the metals come into close contact. Dissimilar metals are, therefore, used—generally cast-iron blocks on steel or wrought-iron tyres. The clean tyre as it revolves is stationary with regard to the rail, and the coefficient there is practically the static. In the following table will be found the results obtained by Galton and Westinghouse [1] for cast-iron blocks upon steel tyres. The coefficient decreases greatly as the speed increases, and also as the blocks become heated after prolonged contact.

TABLE 111. —FRICTION OF BRAKES.

Average Speed.	Co-efficient of Friction between Cast-iron Brake-blocks and Steel Tyres.		
Miles per hour.	1 to 3 seconds.	5 to 7 seconds.	12 to 16 seconds.
0	·408 calcd.	·285 calcd.	·237 calcd.
5	·360 exptl.	...	...
10	·320 ,,	·209 exptl.	...
20	·205 ,,	·175 ,,	·128 exptl.
30	·184 ,,	·111 ,,	·098 ,,
40	·134 ,,	·100 ,,	·080 ,,
50	·100 ,,	·070 ,,	·056 ,,
60	·062 ,,	·054 ,,	·048 ,,

The next table gives the coefficients for steel tyres upon steel rails

[1] *Engineering*, London, Aug. 23, 1878.

TABLE IV.—FRICTION OF WHEEL ON RAIL.

Average Speed.	Coefficient of Friction between Steel Wheel Tyres and Steel Rails.
Miles per hour.	From commencement of Experiment to end of 3 Seconds.
0	·141 calculated.
10	·110 experimental.
15	·087 ,,
25	·080 ,,
35	·051 ,,
45	·047 ,,
50	·040 ,,

Between the brake-block and tyre the friction is high, for there is no foreign substance on the surfaces. In the case of the wheel upon the rail the case is different; here the tyre is slipping over a more or less contaminated surface, and the frictional resistance is smaller. The adhesion of wheels to rails yields a very variable coefficient of friction, ranging roughly from 0·3 to 0·1, according to the state of the weather. Taking the coefficient of the rolling friction of the wheel upon the rail to be 0·2 at all speeds, in ordinary weather at 25 miles per hour we may make the weight upon the blocks equal to the weight of the vehicle, but at higher speeds, say 60 miles per hour, about two and a half times this pressure will, at the moment of application, barely skid the wheels.

On the diagram (fig. 1) some of the figures obtained by Galton and Westinghouse have been plotted with the corresponding theoretical static coefficients. The curves drawn through them are logarithmic curves, the rate at which the friction decreases being approximately proportional to the coefficient of friction at each speed. In other words, the slope of the curve at any point is proportional to the length of the corresponding ordinate, and if the logs. of the ordinates had been plotted the result would have been straight lines.

This decrease of the friction with increasing speed occurs both with the friction between the wheel and rail and with that between the brake-block and tyre. In the former instance, the contact surface of the tyre is constantly passing over fresh rail, which maintains unaltered the nature of the contamination and keeps the temperature from unduly rising; but between the tyre and the brake-block there is no such constant supply of foreign material, and the contact surfaces consequently abrade each other and heat very rapidly. This heating would seem in a great measure to be the cause of the decrease of the friction which occurs when the surfaces have been in contact several seconds.

Laws of Solid Friction.—The laws of solid friction as enunciated by Coulomb are approximately correct for moderate speeds and ordinary loads, but, as they are not applicable at all speeds and loads,
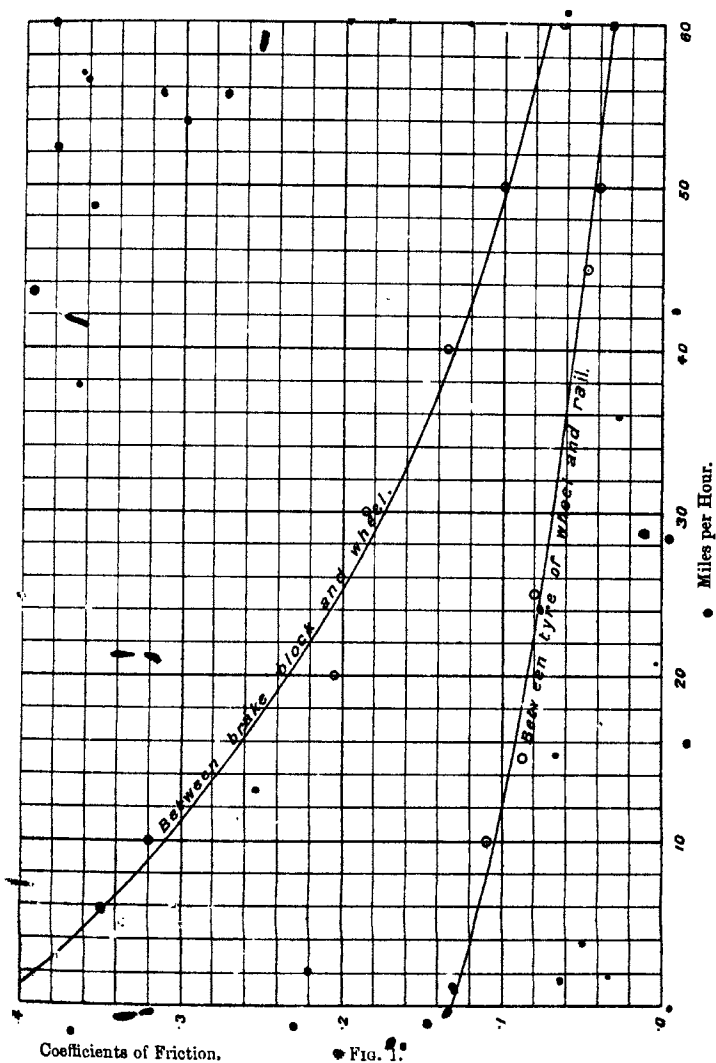
Coefficients of Friction. FIG. 1.

the laws of friction between clean or slightly contaminated surfaces may be more correctly stated as follows :—

1. The frictional resistance is approximately proportional to the load on the rubbing surfaces.

2. The frictional resistance is slightly greater for large areas and small pressures than for small areas and great pressures.

3. The frictional resistance, except at very low speeds, decreases as the velocity increases.

The truth of the first law is easily demonstrated by a machine such as Morin's.

With a slider of cast-iron on a slide of the same metal :—

A weight of 56 lbs. requires 8 lbs. to draw it along.

　　　　　,,　　28　　,,　　4　　,,
　　　　　,,　　14　　,,　　2　　,,

For the coefficient of friction of cast-iron upon cast-iron we have, therefore,

$$\frac{8}{56} = \frac{4}{28} = \frac{2}{14} = \cdot 143 = \mu_1.$$

Rennie obtained ·163 for this coefficient. The value of μ_1 is, therefore, according to these figures, approximately independent of the area of the surfaces and the load, provided abrasion does not take place, but it varies with the condition of such surfaces.

Theory of Solid Friction.—Hele Shaw [1] has attempted to account for the laws of solid friction in the following manner. Supposing the surface to be smooth and worn to their normal condition, there are even then only a certain very limited number of points in contact, and further wear merely removes groups of particles leaving other hollows, or, if no wear is taking place, merely displaces the projecting particles. Any increase of pressure brings a larger number of particles into contact, and so increases, to a proportional extent, the friction, or amount of rubbing and consequent heat produced. Hence the friction varies with the pressure. For low velocities, the constant resistance simply depends on the number of particles in contact, and, as this at any point is the same, the friction is not altered ; when, however, the velocity is very high, it may be that the surfaces are slightly separated, and the friction is thereby reduced ; and it may also be that prominences on one surface periodically displaced, but not permanently removed, may not regain their position with sufficient rapidity to make contact with as many particles on the other surface as they otherwise would.

Rolling Friction.—When a roller passes over an elastic surface the contact is not line contact ; both the roller and the surface upon which it rests are, according to Osborne Reynolds,[2] deformed by the pressure.

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[1] *Cantor Lectures on Friction*, 1886, p. 13.
[2] *Phil. Trans.*, 1876, p. 155.

In fig. 2 an iron roller is represented moving over a surface of rubber. The rubber is distorted by the weight of the roller, and slides or rubs against it at points near C and D. For some distance on each side of the centre, P, there is no slipping, and this area of no slip increases with the friction be-

tween the surfaces. When both the roller and the surface upon which it rests are distorted, the conditions are similar.
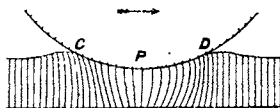
It is conceivable that the use of an unguent for ball or roller bear-ings may so increase the area over

FIG. 2.

which slipping takes place that the resistance to rolling may be actually increased. The lubricant, however, in some measure, pre-vents the wear of the surfaces. In the case of rubber tyres, rolling over rough, uneven ground, such slipping is not large, and the resistance to rolling is correspondingly small.

The laws of rolling friction would appear to be identical with those of sliding friction, with the *proviso* that the resistance varies inversely as the radius of the rolling body. The law may be expressed as follows:—

$$R = \mu_1 \frac{W}{r} \qquad . \qquad . \qquad . \qquad (2)$$

where μ_1 = the coefficient of friction, W = the load on the roller, r = the radius of the rolling body, and R = the frictional resistance.

The rate of slipping at the contact surfaces is so slow that the coefficient of friction, although it probably decreases as the speed increases, does so very slowly.

Cause of Heating.—The energy which is expended in overcoming the frictional resistance of two rubbing surfaces and in keeping them in motion is converted into heat, and raises the temperature of the masses in contact above that of surrounding objects. When the amount of friction is small, the rise of temperature is also small, but should the frictional resistance become large from any cause, the heating of the materials in contact may become so great that the opposing surfaces either become brittle, melt, or even weld together. It is clear that some relationship exists between the work done and the heat produced. The significance of this relationship was first grasped by our countryman, James Prescott Joule, who experimentally demonstrated that a given amount of work, however expended, always produces a fixed quantity of heat. In such cases as the lifting of a weight or the bending of a spring, energy is rendered potential, but this stored energy can likewise produce its proper equivalent of heat.

Before the relationship between work, energy, and heat can be formulated accurately, we must be able to measure both work and heat in some exact manner. The unit of heat used in this country is the quantity which will raise one pound of water, at its maximum

density, one degree F. in temperature. When the C.G.S. or metric system is used, it is the quantity of heat which will raise one gramme of water from $4°$ C. to $5°$ C. Work, on the other hand, is measured by the product of the average resistance and displacement. Thus, in the case of a sliding surface, if the force required to maintain the surfaces in relative motion be one pound, and the distance travelled be 779 [1] feet in each second of time, then the work done each second is 779 foot-pounds. This amount of work has been proved to be just sufficient to raise one pound of water, when at its maximum density, one degree in temperature. 779 foot-pounds is called the mechanical equivalent of heat, and the constancy of its value under all conditions has established on a firm basis the law of the conservation of energy. To the engineer this is one of the most important generalizations ever arrived at, as it affords a ready means of answering many problems which would otherwise be difficult to solve.

    Making W = the total pressure in lbs. on the rubbing surfaces : —
        μ_1 = the coefficient of friction.
        v = the speed of rubbing surface in feet per minute.
    Then, $W\mu_1$ = the frictional resistance.
      $W\mu_1 v$ = the foot-pounds of work done per min.
      $\dfrac{W\mu_1 v}{779}$ = the thermal units generated per min.

We thus see that the heat liberated by any bearing surface is proportional to the friction. In some oil-testing machines the rise of temperature which occurs is measured and is taken as an indication of the resistance to motion which the surfaces offer. The actual rise of temperature depends, of course, not only upon the rate at which heat is liberated, but also upon the conductivity of the heated surfaces. The frictional resistance cannot, therefore, be proportional to the rise of temperature.

    Solid lubricants are all substances, such as graphite, soapstone, etc., which, although they may often be welded into more or less solid masses by pressure, oppose comparatively small resistance to shear,' or to the movement of smooth surfaces in contact with them. They differ in their action from fats and greases, inasmuch as the latter melt and form oils at comparatively low temperatures, whilst the solids referred to maintain their condition unaltered between the surfaces, and prevent seizing or tearing even when the frictional resistances raise the temperature of the bearings very considerably. The coefficient of friction of such lubricants is, however, high, and when economy of power is of consequence, liquid lubricants and a sufficiently large bearing surface should be used, wherever practicable.

    [1] *Phil. Trans.*, 1876, p. 155.

CHAPTER II.

Introductory.—Before mineral oils were introduced as lubricants, engineers had little reason to study the theory of viscosity, or to specify the particular fluidity of the oils they wished to make use of, for the number of animal and vegetable oils available for lubrication is limited, and the degree of viscosity they exhibit does not vary much in different samples, a little experience being usually sufficient to determine the most suitable description of oil for the purpose in view. But since the introduction of mineral lubricating oils, which can be prepared of any desired viscosity, the measurement of this property and the study of its influence upon lubrication have assumed great practical importance.

In this chapter we purpose discussing the nature of viscosity and viscous flow, including the theory of the viscometer. The bearing of viscosity on lubrication will be discussed in Chapter IV. on "The Theory of Lubrication"; and practical viscometry, or the method of measuring the viscosity of lubricating oils, will be reserved for Chapter VI. on "Physical Properties and Methods of Examination of Lubricants."

Nature of Viscosity.—All liquids exhibit viscosity, although in varying degree. Thus, if a vessel of water be tilted and then quickly brought back to its original position, so as to set the water in oscillatory motion, it will be found that with each swing the amplitude of the oscillation diminishes, and that in a very short time the movement dies away or becomes imperceptible, and the surface of the liquid comes to rest in an exactly horizontal position.

If a similar experiment be made with sperm oil, a much greater resistance to movement will be observed; the oscillations produced will not only be much slower, but will also be fewer in number. Very viscous oils, such as castor, and viscid liquids like glycerine and treacle, will not even oscillate; such liquids merely flow steadily until their free surfaces are again horizontal. In all cases the movement ceases sooner or later, and it is the internal friction or viscosity of the liquid which arrests the motion.

Cohesion and Viscosity.—Some writers have assumed a relationship between viscosity and cohesion, but no connection has yet been proved to exist. Considerations such as the following will show that there is no necessary relation between them.

A sphere of soft iron may be slowly rotated around the pole of a powerful magnet with very little difficulty, although considerable force is required to draw the ball and magnet apart. Similarly, the molecules of water move about each other with great freedom, and the liquid has a very low viscosity in consequence ; yet, according to the calculations of Young and Dupré, the force required to tear the molecules apart is equal to a pressure of about 25,000 atmospheres.

Viscous Flow and Lubrication.—As the value of an oil for lubricating depends very largely upon its viscosity, the laws of viscous flow will be considered at some length. We will endeavour to state the mathematics of the subject in as simple a manner as possible, illustrating by means of diagrams those conditions of flow a fairly complete explanation of which is necessary in order to obtain a proper understanding of the part viscosity plays in lubrication.

The conditions of motion of a fluid film enclosed between two relatively moving surfaces differ somewhat from the flow of the same liquid through a capillary tube. In the one instance, we have the conditions obtaining between lubricated surfaces, and in the other, the conditions of flow under which viscosity is most readily and accurately measured.

Viscous Flow between Parallel Horizontal Planes having Differential Tangential Motion.—When a fluid lubricant is interposed between two solid surfaces, one of which is in tangential motion

FIG. 3.

and the other at rest, that portion of the fluid which is in contact with and adherent to the moving surface is constrained to move with it, while that portion which is adherent to the surface which is at rest remains motionless. Between the two surfaces the fluid may be regarded as consisting of a series of superposed layers, each moving at a speed proportional to its distance from the solid fixed surface. This, the simplest form of viscous flow, is illustrated in fig. 3.
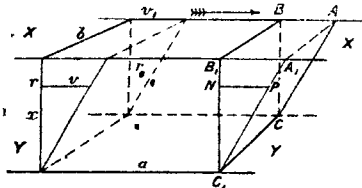
A stratum of a viscous medium is enclosed between two parallel planes, XX and YY, the upper of which is supposed to be moving with uniform velocity in the direction of the arrow, whilst the lower remains fixed. The motion of the fluid must be considered as having reached a steady state, the force producing the motion being supposed to act solely along the plane XX in the direction of the arrow.

The liquid medium may be regarded as made up of a series of infinitely-thin superposed planes (a coarse illustration being a pack of cards), the topmost and lowest of which are held by cohesion in immediate contact with the solid surfaces. The topmost plane of liquid is, therefore, carried along by the moving surface XX, and the lowest plane is held stationary by the fixed surface YY. The intermediate planes of the liquid derive their motion solely from that of the plane XX, the force acting upon which is propagated downwards from stratum to stratum by the internal friction or viscosity of the fluid. As the frictional resistance is absolutely uniform throughout the fluid, each liquid plane must move over the one immediately below it exactly the same distance in the same time ; and, therefore, any row of points in contiguous planos, forming at one moment the vertical straight line C_1B_1, will have moved, after a certain interval, into positions on the inclined straight line A_1C_1. If the length of the line A_1B_1 be taken to represent the velocity with which the upper plane is moving, then the length of the line PN will represent the velocity of the fluid at any point in the plane passing through N. In such a case, which is virtually that presented by a properly lubricated bearing, there is no friction between the two solid surfaces, for they do not touch, and yet force, continuously applied, is required to keep the surfaces in relative motion. The frictional resistance, as already pointed out, is wholly due to the sliding of the liquid layers one over the other, *i.e.* to the resistance offered by the liquid to shear. It has been necessary to deal with this subject in some detail, for the action of a lubricant is sometimes stated to result from the *rolling* of the molecules of the lubricant over each other, and over the solid surfaces between which they pass. Such a view, however, cannot be justified by an appeal to experiment.

The force required to maintain continuous relative motion between opposing plane surfaces, such motion being of the nature of a shearing stress, is measured by the stress per unit area of either of the planes. Thus, we may write

$$F = fA \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where F is the total force, f the force per unit area, and A the area of the planes over which the stress acts.

Since no stresses other than those transmitted by shear act on the mass of liquid abr_0, any section through it parallel to the two bounding planes is exposed to the same stress per unit of area as is the liquid in contact with the planes. If A_1C_1 becomes the position after the lapse of one second of a normal line of section, such as B_1C_1, then the inclination of the line A_1PC_1 will be the same throughout its length, and it must be a straight line. Also the length B_1A_1 represents the velocity of the upper plane, and the length NP the velocity at a distance B_1N from XX.

Hence, since $\dfrac{NP}{NC_1} = \dfrac{B_1A_1}{B_1C_1}$ we may write $\dfrac{v}{x} = \dfrac{v_1}{r_0}$, where v is the velocity at a distance x from YY, and v_1 and r_0 are their values at the surface XX.

The stress f is, therefore, proportional to $\dfrac{r}{x}$, which we may call the rate

of distortion, and we may make

$$f = \eta \frac{v}{x} \qquad . \qquad . \qquad . \qquad (2)$$

where η is a constant which varies with the temperature for any liquid, and is known as the *coefficient of viscosity* of that liquid.

Further,

$$F = fA = fab \quad . \quad . \quad (3) ; \qquad = \eta \frac{v}{x} A \quad . \quad . \quad (4) ; \qquad = \eta \frac{v_1}{r_0} A \quad . \quad . \quad (5)$$

$$\therefore \quad \eta = \frac{F r_0}{v_1 A} \quad . \quad . \quad (6) ; \qquad \text{and } r_1 = \frac{F r_0}{\eta a b} \quad . \quad . \quad (7)$$

Also, the rate of distortion . . . . . $= \frac{v_1}{r_0} \qquad - \frac{F}{\eta A} \qquad . \quad . \quad . \quad . \quad (8)$

Viscosity in Absolute Measure.—If v_1, A, and r_0 are each unity, then $\eta = F$, and the viscosity η of a substance is then measured by the tangential force per unit area of either of two horizontal planes at the unit of distance apart, one of which is fixed, while the other moves with unit velocity, the space between the planes being filled with the viscous substance.

By the establishment of the above simple working definitions we are able to form equations applicable in all problems involving viscous flow

Both in the measurement of the viscosity of various liquids, and in the problems which have to be solved in the theory of lubrication, it is necessary that we should be able to find the volume of the liquid displaced under varying conditions. Although this can be simply accomplished by methods involving the calculus, it is better for the clearer understanding of lubricating problems to attack the matter geometrically.

The volume V swept through by any cross section $B_1B\ C_1C$ in moving to the position $A_1A\ C_1C = \frac{v_1 b r_0}{2}$ . . . . (9)

and this is a measure of the volume of liquid displaced.

Substituting for v_1 its value from equation (7)

$$V = \frac{F r_0^2}{2 a \eta} \qquad . \qquad . \qquad . \qquad (10)$$

and for F its value from (3)

$$V = \frac{f r_0^2 b}{2 \eta} \qquad . \qquad . \qquad . \qquad (11)$$

Viscous Flow under the Action of Gravity between Fixed Planes.—We have hitherto considered only the conditions of flow which result from a stress applied solely at a liquid surface parallel to the direction of flow, the viscosity of the fluid setting in motion the whole mass in such a way that the rate of shear is everywhere the same. But when the liquid flows between two fixed plane surfaces, parallel to each other, and the force setting the fluid in motion acts either upon each particle of the liquid, or equally over the whole of a section normal to the direction of flow, the velocity at different points in the liquid is not proportional to the distance from the solid surface, $\frac{v}{x}$ ceases to equal $\frac{v_1}{r}$, and the rate of shear is not the same at all points.

Although neither in the measurement of the viscous constants of lubricants, nor under the conditions obtaining when lubricants are applied, do we meet with quite the conditions of flow which obtain between stationary parallel planes of infinite width, it is advisable to consider this particular case; for it serves to bridge over the gap between the conditions under which a lubricant really works, and those under which its viscosity is measured.

In fig. 3 the rate of shear, which is the same at all points, is indicated by the slope of the straight line A_1C_1; but when the rate of shear varies regularly across the section the line becomes curved, as is shown in fig. 4, when the viscous liquid is supposed to be flowing between two *vertical* parallel plane surfaces XX and XX, under the influence of uniform pressure acting on the surfaces r_0b, on each side of YY. Here, in place of a force f, acting on unit area of YY, parallel to the direction of motion, we have a pressure p, acting on unit area of the surface br_0, normal to the direction of flow. This force may result either from the pressure of a liquid column, or it may be regarded as the effect of gravity acting with an equal force on each particle of the liquid. In either case the

Fig. 4.

nature of the flow is the same, but it is more convenient to treat it as being due to a pressure p, acting on a surface normal to the direction of flow.
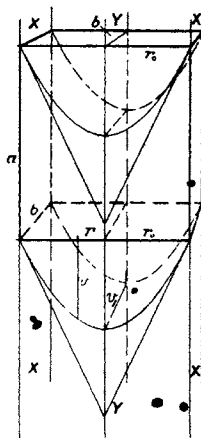
If we take a length a at either bounding plane XX, then the whole pressure on the section br_0 there tends to shear the liquid, the total pressure on half the cross section being pbr_0, and from (8) the rate of shear at the boundary

$$= \frac{pbr_0}{\eta ba} = \frac{pr_0}{\eta a} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (12)$$

We also find that at any distance r from YY the rate of shear $= \frac{pr}{\eta a}$. (13)

and we see that the rate of shear is directly proportional to the distance r from the plane YY. That is to say, at any point C (fig. 5) in the liquid the rate of shear is proportional to BC. Now $\frac{AB}{BC}$ is the rate of shear, CA being tangential to the curve at C. Draw CD perpendicular to CA, to cut the centre line in D. Then we have $\frac{BD}{BC} = \frac{BC}{BA}$. But $\frac{BC}{BA}$ is proportional to $\frac{1}{CB}$ (see above). Therefore $\frac{BD}{BC}$ is proportional to $\frac{1}{BC}$ or BD is constant.

But BD is the subnormal of the curve $C_1E_1C_1$, which can easily be shown to be a parabola, and therefore the volume of fluid passed on each side of YY, in unit time, is half the volume of a parabolic prism $C_1E_1C_1$ of length b.

Fig. 6.

Fig. 6.
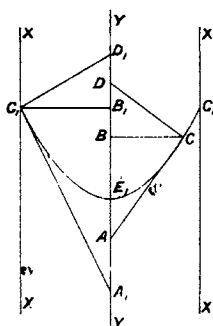
Now, since the curve is a parabola,

$$B_1E_1 = \tfrac{1}{2}B_1A_1,$$

and, from equation 12,

$$\frac{B_1A_1}{B_1C_1} = \frac{pr_0}{\eta a};$$

therefore,

$$B_1A_1 = \frac{pr_0^2}{\eta a}$$

and

$$B_1E_1 = \frac{pr_0^2}{2\eta a} \qquad . \qquad . \qquad . \qquad . \qquad (14)$$

Now, the volume enclosed by the parabolic curve $C_1E_1 = \tfrac{2}{3}$ the area of the base × the perpendicular height.

Therefore, the volume passed in unit of time on each side of the plane YY

$$= \tfrac{2}{3} \times r_0 b \times \frac{pr_0^2}{2\eta a} \qquad . \qquad . \qquad . \qquad . \qquad (15)$$

$$= \frac{pr_0^3 b}{3\eta a} \qquad . \qquad . \qquad . \qquad . \qquad (16)$$

and the volume passed in any given time (t) will be

$$\frac{pr_0^3 bt}{3\eta a} \qquad . \qquad . \qquad . \qquad . \qquad (17)$$
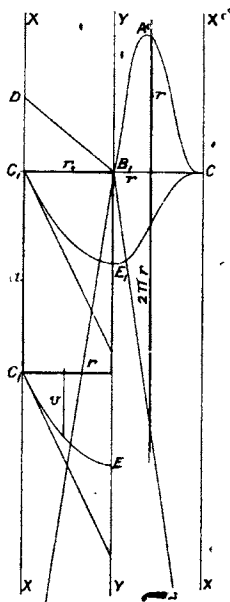
Viscous Flow through Capillary Tubes.—As will be seen when the theory of lubrication comes to be discussed, the conditions of viscous flow obtaining between plane surfaces are all important. Still such conditions are not those under which the coefficient of viscosity η is most accurately and easily measured. The most concordant values have been obtained by measuring the rate of flow through capillary tubes in which, as between plane surfaces where the flow results from the pressure of a given head of liquid, the rate of shear is greatest at the bounding surface.

Fig. 6 shows diagrammatically the conditions of flow obtaining in a capillary tube, at a point some distance from the end at which the liquid enters, the flow having reached a state of equilibrium ; for at the inlet end the effects of inertia manifest themselves.

In a portion of tube of length a, the whole pressure on the cross section C_1C tends to shear the liquid at the bounding surface, and the area over which this pressure acts is equal to $2\pi r_0 a$. Now, the area of the cross section of the tube $= \pi r_0^2$. Therefore, the total pressure over the cross section

$= p\pi r_0^2$, and from (8) the rate of shear at the boundary $= \dfrac{p \times \pi r_0^2}{\eta \times 2\pi r_0 \times a}$

which resolves itself into $\dfrac{pr_0}{2\eta a}$ . . . . (18)

In the case of a small cylinder of liquid concentric with the tube and of radius r, the rate of shear at its boundary $= \dfrac{pr}{2\eta a}$ . . . . (19)

Therefore, the rate of shear is directly proportional to the distance from the centre line of the tube, and the curve indicating the rate of distortion is, as in the case of the parallel planes, a parabola ; and the volume passed in unit of time is the volume of a paraboloid of revolution, having a base of radius r_0 and a height $= B_1E_1 = \frac{1}{2}B_1A_1$ (fig. 5).

From (18) we have

$$\frac{B_1A_1}{B_1C_1} = \frac{pr_0}{2\eta a} \qquad (20)$$

Therefore,

$$B_1A_1 = \frac{pr_0^2}{2\eta a} \qquad (21$$

and

$$B_1E_1 = \frac{1}{2}B_1A_1 = \frac{pr_0^2}{4\eta a} \qquad (22)$$

Now the volume of a paraboloid of revolution $= \frac{1}{2}$ the area of the base $\times$ the perpendicular height. Therefore, the volume passed in unit time

$$= \frac{1}{2} \times \pi r_0^2 \times \frac{pr_0^2}{4\eta a} \qquad (23)$$

or

$$\frac{\pi}{8} \cdot \frac{pr_0^4}{\eta a} \qquad (24)$$

And the volume V passed in any given time $= \dfrac{\pi}{8} \cdot \dfrac{pr_0^4 t}{\eta a}$ . . . (25)

We may find an expression for the viscosity of the liquid from the above,

by substituting for p its equivalent in terms of the' head and density of liquid, and the force of gravity, *i.e.*,

$$\lambda \qquad \eta = \frac{\pi g p h r_0{}^4 t}{8 V_a} \qquad . \qquad . \qquad . \qquad . \qquad (26)$$

Poiseuille was the first to demonstrate experimentally that the volume of liquid passed by a capillary tube is directly proportional to the pressure urging it along, and to the fourth power of the radius of the tube, and inversely as its length. On this account the above is known as *Poiseuille's formula*, and may be used, after making a small correction for h, for the purpose of calculating *absolute* viscosities.

Physical and Mechanical Viscosity. —As Osborne Reynolds has pointed out,[1] it by no means follows that for each particular liquid a fixed value of η need necessarily exist, such that f calculated by equation (2) agrees with the values of f determined by experiment for all values of v and r_0. As a matter of fact experiment shows that liquids have apparently two viscosities ; for, as is well known to engineers, in large pipes the resistance to flow varies as the square of the velocity, and not directly as the velocity. When such is the case, η is not constant in value.

Carefully conducted experiments by Coulomb, Poiseuille, and others, on the rate of flow through long capillary tubes, have proved conclusively that the resistance under certain conditions is proportional to the velocity, and that η has then a constant value. Poiseuille's experiments also proved that the volume passed varies as the fourth power of the radius of the tube. Such being the case, we may safely regard the flow of liquids through tubes of very small bore as being controlled by the physical viscosity of the liquid, and use equation 26 as a means of calculating the value of η when the other values have been determined experimentally. But the fact must not be lost sight of, that to obtain a correct result, the size of the tube, the intensity of the pressure producing the flow, and the viscosity of the liquid, must bear certain relations to each other. The reasons for this have been successfully worked out by Osborne Reynolds, who demonstrated that the two viscosities, physical and mechanical, result from a change in the character of the flow from that of direct parallel to that of sinuous or eddying motion.

To show this change in the nature of the flow when the velocity reaches a certain value, a long, bell-mouthed glass tube was immersed horizontally in a tank of water. One end of the tube passed through the side of the tank and was bent vertically downwards for several feet, being terminated by a stop-cock. By partially opening or closing this cock, the water could be made to flow through the tube at any desired speed. Terminating opposite the bell-mouthed tube, and immersed in the water, was fixed a much smaller tube through which a highly coloured stream of water was discharged. When the speed of flow was small, the coloured stream passed through the whole length of the bell-mouthed tube as a perfectly straight line

[1] "Theory of Lubrication," *Phil. Trans.*, 1886, p. 165.

(fig. 7). When, however, by opening the cock, the speed reached a certain value, the band of colour suddenly broke up and discoloured the whole of the liquid. By the intermittent light of an electric
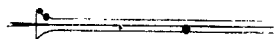
FIG. 7.   FIG. 8.

spark, the mass of colour resolved itself into a series of more or less distinct curls, showing eddies, as in fig. 8.

A series of experiments made it clear that so long as the flow remained direct and steady, the resistance varied directly as the velocity, but as soon as the critical speed was reached the resistance became proportional to the square of the speed, or thereabouts, and sinuous motion was set up. The critical speed was found to vary directly as the viscosity, and inversely as the diameter of the tube and the density of the liquid.

Although it is an experimentally ascertained fact that there is a certain critical speed for each size of tube and each liquid, below which the resistance varies directly as the velocity, and above which the resistance is proportional to the square of the velocity, the reason for the change in the nature of the flow has yet to be satisfactorily explained.

We have thus two essentially distinct viscosities; the one a mechanical viscosity, arising from the irregular motion of the fluid, and the other a true physical property of the fluid depending in some way upon its structural peculiarities. Although the value of the physical viscosity determines in some measure which of the viscosities shall control the flow of the fluid, when the flow is once in accordance with the mechanical viscosity the physical viscosity does not in any direct way show itself. Thus, when in a particular tube the velocity of oil or treacle is sufficient for the resistance to vary as the square of the velocity (i.e. for the liquid to flow with sinuous motion) the resistance is practically the same as it would be with water at the same velocity, although the physical viscosity of water may be more than a hundred times less than that of the oil.[1]

The critical velocity is rarely if ever reached by lubricating films, and when the lubrication is perfect, the resistance to relative motion is due to the physical viscosity of the lubricant.

The possibility of slipping at the boundaries, or of internal disruption, must not be lost sight of. So far, no indication of this has been perceived, either in water or liquid lubricants, even when the tangential stresses to which they have been subjected in narrow channels have been as high as 0·702 lb. per square inch.

Determinations of viscosity made by measuring the resistance offered to the motion of discs or cylinders immersed in liquids are, for the most part, unsatisfactory. In such cases turbulent motion

[1] Osborne Reynolds, *Phil. Trans.*, 1895, p. 153.

is locally, if not generally, set up, and the results are misleading. For this reason such methods of measuring, or attempting to measure, the viscosity need not be referred to here.

Effects of Temperature and Pressure.— With rise of temperature the viscosity of liquids decreases—sometimes very rapidly. In this respect liquid lubricants differ greatly from each other. Oils of animal and vegetable origin retain their viscosities better than those of mineral origin, but they all become very mobile with rise of temperature, and lose, in a great measure, their lubricating value. Not only is it necessary, therefore, to keep a liquid, whilst testing it, at a very uniform temperature, but the effect of varying temperature must be carefully observed.

Viscosity varies also with pressure, water having its viscosity decreased by this means. On the other hand, concentrated solutions of common salt have their viscosities increased by pressure, as has also oil of turpentine. No experiments, however, seem to have been made to ascertain the changes of viscosity which lubricating oils undergo when under great and varying pressures. Such information would be valuable, since lubricating films are frequently subjected to very considerable loads.

Conditions determining Steady Flow.—The formulæ obtained for the flow of liquids through capillary tubes only hold good, as we have seen, so long as the flow is direct and not sinuous. When high pressures and comparatively short tubes of large bore are employed, the liquid, if not very viscous, ceases to flow steadily in paths parallel with the bounding walls ; the motion becomes sinuous, and the resistance offered to the flow of the liquid ceases to be directly proportional to the velocity. The length and diameter of the capillary tube, and the pressure with which a liquid (of given viscosity and density) is forced through it, must therefore be properly proportioned to each other, or the physical viscosity cannot be even approximately determined.

Osborne Reynolds[1] has found that for the flow to be steady the product of the mean velocity $\bar{v}$, the radius of the tube r_0, and the density of the liquid ρ, divided by the viscosity η, must—in the case of a round tube—be less than a certain constant c.

$$\frac{r_0 \bar{v} \rho}{\eta} < 700 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (27)$$

This constant (700) is the same whatever system of weights and measures be adopted, for the divisor and dividend each involve the same powers of length, mass, and time.

When the value of c is less than 700, the volume of liquid passed is, as already demonstrated, $\dfrac{\pi}{8} \cdot \dfrac{h \rho g r_0^4 t}{\eta a}$

and the mean speed of flow $\bar{v} = \dfrac{V}{\pi r_0^2 t} = \dfrac{\pi}{8} \cdot \dfrac{h \rho g r_0^4 t}{\eta a \pi r_0^2 t}$

$$= \frac{h \rho g r_0^2}{8 \eta a} \qquad . \qquad . \qquad . \qquad . \qquad (28)$$

[1] *Phil. Trans.*, 1895, p. 149.

Substituting in equation (27) the value of $\bar{v}$ in equation (28) we have

$$\frac{r_0^3 h \rho^2 g}{8 \eta^2 a} < 700 \qquad . \qquad (29)$$

and

$$\frac{h g r_0^i}{a} < 5600 \frac{\eta^i}{\rho^2} \qquad . \qquad . \qquad . \qquad (30)$$

Unless the proportions of the viscometer, and the physical properties of the liquids used in it, be in accordance with the requirements of this equation, the flow will be unsteady, and the true viscosity cannot be calculated. When absolute viscosities are desired, the viscometer should be designed so as to make the value of c as small as possible.

But sinuous motion, even when c is very much greater than 700, does not set in, as will be seen from fig. 8, immediately the fluid enters the tube. With tubes having trumpet-shaped orifices the disturbances appear and the flow becomes sinuous at about thirty diameters from the end; but when the end is flat the disturbances approach the inlet end more closely. The flow of liquids in very short tubes is, therefore, free from eddies, even though the viscosity of the liquid, the diameter of the tube, and the rate of flow may be such as to make c greater than 700. In such cases, although the flow is steady throughout the tube for some distance from the inlet, the velocities are not such that the rate of distortion is proportional to the distance from the centre. Such short tubes may, therefore, be used to obtain comparative, but not absolute, viscosities, even with very mobile liquids. The conditions which determine whether the flow shall be steady or unsteady are often very complex, for the stream lines may be parallel, as in tubes or between parallel surfaces; convergent, as in a conical mouthpiece; or divergent, as in the latter case when the motion is reversed.

The circumstances which conduce to a direct steady motion are— (a) high viscosity or fluid friction : (b) a free surface as in a fountain jet ; (c) solid converging boundaries ; and (d) curvature, with the velocity greatest outside.[1]

The circumstances which conduce to sinuous motion are—(a) particular variation of velocity across a stream, as when a stream flows through still water; (b) solid bounding walls : (c) solid diverging boundaries ; and (d) curvature, with the velocity greatest inside.

Energy of Flow through Capillary Tubes.—When the coefficient of viscosity is calculated from Poiseuille's formula (26), it is assumed that the character of the motion is the same at all sections of the tube, and that all the energy supplied to the liquid is converted into heat within the tube. But the coefficient so obtained is only approximately correct, for not only is there some resistance to the flow of the liquid outside the tube, but the steady condition of flow within the tube is not reached until the liquid has travelled some distance from the orifice. The liquid, when it approaches the critical speed, often possesses considerable velocity, and an appreciable amount of energy then exists as kinetic energy in the issuing fluid. As this energy results from the pressure due to the head of liquid, a deduction on this account should be made if accuracy is aimed at.

We have, consequently, four sources of error to consider and, if

[1] *Proc. Royal Institution*, 28th March 1894.

possible, to allow for—(a) external viscous resistance in the liquid at the ends of the tube; (b) abnormal conditions of flow at inlet end of tube; (c) surface tension effects at discharge orifice; and (d) energy of flow at point of discharge. No corrections have yet been devised for a and b. They are small and become practically negligible when the tube is long; but when the tubes, compared with their diameters, are so short that sinuous motion is not set up, even when the value of c is much greater than 700, the necessary correction often becomes so large that the true viscosity cannot be calculated even approximately. Neither can an allowance for d be made, for a state of equilibrium is not reached even at the end of the tube, and the energy of flow cannot be found.

The third source of error (c), however, is of some importance, and is sometimes met by so designing the viscometer that the discharge end of the capillary tube is always immersed in the liquid. An allowance on this head is difficult to make when the liquid flows directly into the air from the orifice, for its value depends upon the curvature of the liquid surface as well as upon the actual tension of the surface, i.e. upon the dimensions of the drops, or upon the form of the liquid stream and the surface tension of the liquid.

The fourth (d) is important, and can be accurately determined when the tube is long and a steady condition of flow is set up, for there is no reason to suppose that any change takes place in the distribution of energy as the discharge orifice is approached.

Correction for Energy of Flow.—That a correction for the energy of flow is necessary was pointed out by Hagenbach,[1] and his method of measuring it has been very generally followed. Lately, however, Wilberforce [2] has demonstrated that the correction suggested by Hagenbach is too small, and that the true correction is furnished by deducting from the mean head, h, a quantity $= \dfrac{\bar{v}^2}{g}$, where $\bar{v}$ is the mean velocity of flow through the tube. A geometrical method of demonstrating this is shown in fig. 6, in which the ordinates of the parabolic curve $C_1 E_1$ give the velocities of flow at any distance from the centre line. If they be regarded as representing the successive values of $\dfrac{v}{v_1}$, where v_1 is the maximum velocity, then $B_1 E_1$ is equal to unity on this scale.

The curve CE_1 is plotted on the same scale to represent the corresponding values of $\left(\dfrac{v}{v_1}\right)^3$; and finally the ordinates of the curve $B_1 AC$ are made proportional to $\left(\dfrac{r}{v_1}\right)^3 2\pi r$. The ordinates of $B_1 D$ are equal on the same scale to $\left(\dfrac{v}{v_1}\right)^3 2\pi r$.

Now, if we consider a thin cylinder of liquid of radius r, length a, and thickness τ, its energy is

$$\frac{2\pi r a \tau v^3}{2g}$$

[1] Pogg. Ann., 1860., cix.   [2] Phil. Mag., May 1891.

and is, therefore, proportional to the area of the part of the curve B_1AC included between the corresponding ordinates.

Hence, the total area of the curve B_1AC is proportional to the energy of flow, and in the same way it can be shown that B_1C_1D would be proportional to the energy of flow if the velocity were constant across the section. If the areas B_1AC, B_1DC_1, be now measured up with a planimeter, B_1AC will be found to be equal to just twice B_1DC_1. Hence, the true energy of flow is equal to twice that obtained on the assumption that the velocity is uniform all over the section.

In this latter case, the correction would evidently be $-\dfrac{\bar{v}^2}{2g}$. Hence the true correction is $-\dfrac{\bar{v}^2}{g}$, as shown by Wilberforce and others.

When all the values required for calculating the viscosity by Poiseuille's formula (26) are known, the deduction necessary in the value of h is easily obtained, for

$$\bar{v} = \frac{V}{t\pi r_0^2} \qquad \cdot \qquad \cdot \qquad \cdot \qquad \cdot \qquad (31)$$

Substituting this value for $\bar{v}$ we obtain

$$\frac{V^2}{g\pi^2 r_0^4 t^2} \qquad \cdot \qquad \cdot \qquad \cdot \qquad (32)$$

as an expression for the required correction.

Viscometer Proportions.— In order to obtain the value of η with accuracy, it is necessary that the correction for energy shall be small—say one or two per cent. A formula for calculating this percentage is obtained as follows:

The energy correction being equal to $\dfrac{\bar{v}^2}{g}$

$$h : \frac{\bar{v}^2}{g} :: 100 : \%$$

Therefore,

$$\frac{100\bar{v}^2}{hg} = \%.$$

Substituting for $\bar{v}^2$ the value from (28)

$$\frac{100q^2\rho^2h^2r_0^4}{64\eta^2a^2hg} = \frac{100g\rho^2hr_0^4}{64\eta^2a^2} = 1.563\frac{g\rho^2hr_0^4}{\eta^2a^2} = \%.$$

Inlet End Resistance.— This disturbing factor has not yet received anything like complete experimental treatment.

Fig. 9 shows the inlet end of a capillary tube into which a liquid is flowing. The speed of flow everywhere decreases as we leave the centre line, and increases as the orifice is approached. The liquid is consequently undergoing shear, both inside the tube and outside near its ends, and the resulting resistance must be added to that in the tube if we are to obtain the true viscosity. This resistance, and that due to the abnormal conditions of flow just inside the tube, we may allow for by somewhat increasing the length of a. Some experiments, the results of which we shall give when we come to deal with practical viscometry, and which were made for the purpose of calibrating viscometers having short capillary tubes, show that when the rate of flow is so slow that the energy correction is negligible, the viscosity, calculated by Poiseuille's formula, is somewhat greater than
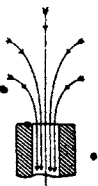
FIG. 9.

experiment with very long tubes proves it to be. * The value we obtained for water at 20° ℃., using a viscometer with a long and narrow bore, is about 2 per cent. greater than that obtained by Thorpe and Rodger.[1]

Plastic Friction.—Plastic substances, such as tallow, lard, moist china-clay, etc., differ from viscous fluids inasmuch as they require that the shearing stress shall reach a certain value before continuous shear takes place. They can, therefore, permanently retain their shapes when the stresses are unequal in different directions; *i.e.* they can transmit stresses without undergoing continuous shear. Sometimes the plastic yield-point is very low, and the substance behaves much as does a viscous liquid. A layer of lard, for example, placed between two smooth surfaces, which are prevented thereby from touching, requires the exercise of a definite stress to cause tangential motion ; but when once relative motion is set up by the action of a sufficiently powerful force, the resistance increases with each increase in the rate of shear. In the case of plastic friction, therefore, we have something corresponding to the static friction of solid surfaces in contact ; but whether the plastic yield-point varies with the pressure normal to the direction of flow (shear), or whether the resistance is proportional to the rate of shear, is uncertain.

The distinction between plastic or soft solids and viscous ones was clearly recognized by Maxwell.[2] He says : "When continuous alteration of form is only produced by stresses exceeding a certain value, the substance is called a soft solid, however soft it may be. . . . Thus, a tallow candle is much softer than a stick of sealing-wax ; but if the candle and the stick of sealing-wax are laid horizontally between two supports in summer, the sealing-wax will, in a few weeks, bend with its own weight, while the candle remains straight. The candle is, therefore, a soft solid, and the sealing-wax a very viscous fluid."

It is evident that the same substance, for instance, lard or tallow, may act when in use either as a plastic lubricant or a viscous one, for at moderately high temperatures these substances melt, and may become viscous lubricants, *i.e.* true oils.

At first sight it would seem that the resistance to shear offered by a plastic substance would be so great that it would be altogether unsuitable for lubricating purposes. But such is by no means the case ; indeed, at very low speeds the resistance to motion of a film of plastic grease is often smaller than that of an oil film, for the grease film is much thicker, and the rate of distortion is less.

When two surfaces are forced together between which there is a plastic substance, the pressure or stress is transmitted from point to point, shear takes place, and the intervening lubricant is expelled. A viscous liquid under such conditions is expelled until the bearing surfaces come into contact, or the surface forces prevent further escape. Such, however, is not the case if the intervening lubricant be plastic,

for the nearer the surfaces approach, the less the shearing stresses become, and long before the surfaces can touch they reach the plastic yield point, and further flow ceases.

In fig. 10 are shown the experimentally ascertained curves of shear for plastic clay. Here the surfaces AB and CD are approaching each other without tangential motion. The curves showing the conditions of distortion will be seen to differ remarkably from those of a viscous fluid, which take the form of parabolas (fig. 28, p. 67).

Unfortunately, there is very little experimental data to guide us
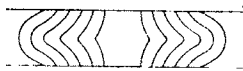
Fig. 10.

here, except such as is furnished by the actual working of vehicles lubricated by greases. This aspect of the question can be more satisfactorily discussed when we come to deal with the t' eory of lubrication, for, as we have pointed out, the actual resistance to motion offered by oil and grease films depends upon their thickness, area, and the temperature produced by the friction, as well as upon the absolute viscosity or plasticity.

Many of the greases used for lubricating purposes are mixtures of soft solids and viscous oils or soaps. On standing, the oils sometimes separate out from the solids as minute globules, suspended in a solid matrix. When kneaded, however, the oil is spread out and forms continuous films, which much reduce the resistance to shear.

CHAPTER III.

Lubrication and Superficial Tension.— *Introductory.*—Although Osborne Reynolds[1] has proved that the results obtained by Beauchamp Tower[2] with perfectly lubricated journals were entirely due to the viscosity of the oils employed, it has become clearly recognized by engineers that when the supply of oil is insufficient for perfect lubrication, and when the rate of friction is very slow, or the load excessive, lubrication depends upon other less generally understood and somewhat obscure properties. As a matter of fact, a liquid may have the required viscosity and yet not be a lubricant. J. Veitch Wilson states that *body* or viscosity is not the only property by which the antifrictional value of an oil is determined. The differentiating principle must, he urges, be attributed to some other property. Thurston states that a liquid, to act as a lubricant, must possess "enough 'body' or *combined capillarity and viscosity* to keep the surfaces between which it is interposed from coming in contact. . . ." Although he does not substantiate this statement in detail, there is every reason for regarding it as true, if not taken too literally.

To be lubricants, liquids and soft solids should feel oily or greasy. As capillarity, oiliness, greasiness, wetting, emulsification, etc., are either wholly or in part phenomena resulting from superficial tension, this property will be dealt with at some length, so far as it seems to throw light upon lubrication problems; for the phenomena resulting from superficial tension are among the most interesting and important that can engage the attention of either the chemist or the engineer, and they manifest themselves in a great variety of ways. Unfortunately, the values of many of the physical constants a knowledge of which is required—such as the thickness of various liquid films when spread over or between solid surfaces—have not in many cases been measured.

Lubricating Films.—When a glass surface is rubbed by a wet

finger, care having been taken to remove all grease, the friction between the skin and the glass is very considerable. If the surface be the edge of a wine glass, the alternate seizing and freeing of the contact surfaces causes the glass to vibrate and produce a musical note. Even such a thick liquid as glycerine, when the rubbing movement is slow, fails to keep the surfaces apart and prevent the glass from feeling harsh. A little grease, fat, or good lubricating oil will, on the other hand, remain as a fairly thick film between the surfaces, and enable them to slip freely over each other, even at low speeds.

We may, therefore, take it that a film of pure water between two solid surfaces is so thin that it fails entirely to keep their asperities from interlocking ; whereas lubricating oils form films on such surfaces which succeed, more or less, in preventing the surfaces from seizing, and so greatly reduce the friction between them.

In many respects, the property which some liquid films possess of powerfully resisting all attempts to reduce their thicknesses below certain fixed values, and even, as we shall see, of preventing bubbles from bursting, is a most valuable one. It is evidently in no direct way dependent on viscosity, for many very viscous liquids fail entirely to form lubricating films. Nor is it measured by the superficial tension of the liquid. All we have a right to say is[1] that when the superficial tension of the lubricant is less than that of the solid, the liquid spreads itself over the surface of the latter, and when it has so covered the surface, its lubricating value depends upon the thickness of the layer it forms, and the extent to which it resists efforts made to expel or extrude it.

Soap (Bubble) Films.—If the looped end of a piece of wire be dipped into a solution of soap and water and then removed, there will be seen stretched across the loop a thin diaphragm of liquid. Such a film possesses considerable elasticity and strength, as may be proved by placing upon it a small moistened wire ring, which it supports without breaking. In other words, the film resembles a sheet of indiarubber, some force being required to stretch or distort it. Vernon Boys[2] has described a number of very beautiful experiments, illustrating the tension properties of such liquid films. He used for this purpose a mixture of 1 part, by weight, of sodium oleate, dissolved in 40 parts of distilled water. When solution was complete, one-third of its volume of glycerine was added to the liquid, and the whole was allowed to settle. The liquid was then siphoned off from the impurities which had risen to the surface, and was clarified by the addition of a few drops of ammonia. Films made of this mixture last a very long time, and very instructive studies of superficial tension phenomena may be made by their means. Such films consist of two surface layers which have closed together by the withdrawal of the water from between them, and each layer is under the same degree of stress. The surfaces of all liquids exhibit allied phenomena.

Wetting of Solid Surfaces.—A slip of clean glass dipped into a

[1] See p. 37.   [2] *Phil. Mag.*, May 1888, p. 409.

vessel of water, and then withdrawn, will be found to have a thin film of water adhering to it. The film so formed consists of two surface layers, one in contact with the air and the other in contact with the glass. In this case, the mass of glass plays the same part as the air in a bubble. If the plate be held vertically and partially immersed in a vessel of clean water, the external surface layer of the film on the glass becomes continuous
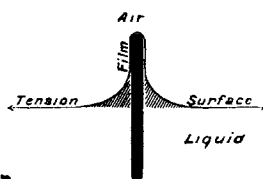
FIG. 11.

with the surface layer of the water, and it will be observed that the water surface, where it meets the solid, is distorted, as shown, exaggerated, in fig. 11.

Here the surface layer of the liquid in the vessel is in a state of tension, the external surface layer on the raised glass plate is in a similar state of tension, and the two stresses are acting at right angles to each other. To balance these tensions a small quantity of water, shaded in the figure, is lifted above the general level, and the free surface becomes curved. The weight of the water or other liquid raised is proportional to the superficial tension of the vertical surface layer or film, which covers the glass and is in contact with the air, just as the load on a spring-balance is proportional to the stress on the spring.

The superficial tensions of different liquid surface films vary very considerably, that of mercury being greater than that of water, whilst the superficial tension of the latter is greater than that of oils.

Stability of Liquid Films.—Very little is known concerning the thickness or viscous properties of liquid films, other than can be gathered from friction phenomena. For example, the experiments of Thurston[1] on the static friction of surfaces lubricated with lard oil and sperm oil would seem to prove that although the former is nearly twice as viscous as the latter, the lard oil gives the smallest coefficient of friction, and therefore must form the thickest lubricating film.

A difference has also been noticed in the relative stability of bubbles blown with different liquids. Pure water, for example, will not form permanent bubbles—the film rapidly gets thin in places and bursts, owing to the superior tension of the surrounding parts. On the other hand, when soap is added to the water the film refuses to be reduced to a thickness of less than twelve millionths of a millimetre, for with decreasing thickness its strength increases. This minimum thickness of a soap film is sufficient to prevent polished surfaces separated by it from touching each other except at a few points and, therefore, constitutes it a lubricant.

Reinold and Rücker[2] have studied the properties of soap films with great care. When first formed, the surfaces enclose a con-

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[1] *Friction and Lost Work*, third edition, p. 316.
[2] *Phil. Trans.*, 1883, p. 645, and 1886, p. 627.

siderable volume of liquid which does not in any way affect the
tension of the surface layer, and when this portion of the liquid has
drained away, the film remains at a constant thickness of about
twelve millionths of a millimetre. At this figure the surfaces may be
considered to have closed together, and the films look black all over,
for they reflect very little light and have ceased to show Newton's
rings. The stability and uniform thickness of these thin films indi-
cate that, when a certain minimum thickness has been reached, the
tensile strength increases and prevents rupture.

The majority of even very viscous mineral oils are deficient in
oiliness, for they do not form films sufficiently thick to keep the
static friction as low as can be obtained by using animal or vegetable
lubricants. This has led to the manufacture of 'blended' and soap-
thickened oils. The former are mixtures of mineral with animal and
vegetable oils. The latter contain metallic soaps, which are supposed
to act by increasing the viscosity, but which may have the same
effect upon mineral oils as on water, i.e. they may cause them to
form thick lubricating films instead of thin ones.

Experiment only can determine whether the latter mixtures are
really useful ; the substances added are not always adulterants, but
rather ingredients added for the purpose of conferring upon the
lubricants properties in which they are deficient.

Theory of Superficial Tension. — *Molecular Attraction.*—Some
reasons have already been adduced in support of the view that the mole-
cules of solids powerfully attract each other when brought into close
juxtaposition. This is equally true of the molecules of liquids, which,
in spite of their fluidity, require the expenditure of a considerable
amount of energy to separate their molecules completely. At sensible
distances the attractive forces between molecules are inappreciable,
but when the distances separating them become infinitesimal the
forces become extremely powerful. It has been computed that such
attractions become perceptible when the distances separating the
molecules are reduced to $\frac{50}{1,000,000}$ millimetre (Quincke).

Berthelot found that water could sustain a tension of about 50
atmospheres, applied directly, and the phenomenon of retarded ebulli-
tion, described by Dufour, helps to confirm this view. In a vessel
containing a mixture of linseed oil and oil of cloves, the latter observer
immersed drops of water, which were still seen to be swimming about
after the temperature had been raised to 356° F. The pressure of
aqueous vapour is, at this temperature, nearly ten atmospheres, or
about 147 lbs. per square inch. Hence, the cohesion of the water must
be able to support a tension of at least 132 lbs. per square inch. In
these experiments, the water was carefully freed from dissolved air, etc.

Intensity of Molecular Stresses.—Evaporation or boiling may be
regarded as a process in which the cohesive forces of the molecules of
the liquid have been completely overcome, the heat rendered latent
being a measure of these forces. This view Lord Rayleigh [1] regards as

substantially sound, and he calculates that, on this hypothesis, the cohesive force of water is 25,000 atmospheres.

Lord Kelvin has pointed out[1] that the experimentally ascertained attractive forces are millions of times greater than would follow from the law of gravitation, on the supposition that matter is perfectly homogeneous; but as we know that matter is not perfectly homogeneous, by postulating sufficient heterogeneity, the attractive forces *may* be accounted for without assuming any attractive force other than that in accordance with Newton's law.

It is admitted that, as there is every reason to believe that the atoms and molecules never come into actual contact, this attractive force, which is operative over a limited range, must be balanced by a repulsive force of suitable intensity, operative over a different range; consequently, the molecules approach each other until their attractive and repulsive forces are in equilibrium.

Condition of Surface Molecules.—It is clear that the molecules in the interior of a liquid are attracted by other molecules on all sides. On the other hand, the molecules at or very near the surface are differently situated, for the attractive forces are then by no means equal in all directions. In other words, the molecules at or very near the surface have their attractive forces only partially satisfied, and the unbalanced stresses are constantly tending to reduce their number and, therefore, to decrease the surface area. Any increase of the surface area involves an increase in the number of molecules whose attractions are not satisfied, and to effect this, force must be exerted. We thus have all liquid surfaces tending with considerable force to contract their areas, and exhibiting the phenomenon of superficial tension. The resultant effect of the mutual attractions between different portions of a fluid really gives the same result as would be obtained if the liquid were "absolutely deprived of the attractive forces of its molecules, and its whole surface were coated over with an infinitely contractile film, possessing a uniform contractile force."[2] This is a convenient way of explaining the fact that a mass of liquid, left entirely to the action of cohesive forces, assumes a spherical figure, but it is important not to lose sight of the fact that the spherical form is the result of an endeavour of the particles to get as near to each other as possible.

Liquid Interfaces.—But even when we have the surfaces of two different liquids in contact, the molecular stresses may not be completely satisfied, for the ranges and intensities of the attractive and repulsive forces of the two kinds of molecules may be very different. There, consequently, remain unbalanced forces, and the interface is in a condition of strain.

Lord Kelvin, who carried out a number of experiments on the behaviour of dissimilar liquids when in contact, found it convenient to employ carbon disulphide and a solution of zinc sulphate as no

[1] *Popular Lectures and Addresses*, vol. i. p. 59.
[2] Kelvin, *Popular Lectures and Addresses*, vol. i., 1891, p. 16.

immediate chemical or physical action results on bringing such liquids together. Additional advantages are e from the fact that carbon disulphide assumes an intense violet coloration with iodine, which enabled observations to be more readily noted; while the zinc sulphate solution could be adjusted to any required density. When both liquids were of the same density, it was found that globules of either suspended within the other assumed a spherical condition, as the result of the tension developed at their surfaces of contact.

Miscibility of Liquids.—At present, our knowledge of the conditions which determine whether two given liquids will diffuse into each other, or remain apart, is very limited; indeed, a knowledge of their comparative surface tensions affords us little or no help in this direction. Two drops of mercury, for instance, have the same surface tension. The tension, however, of the junction surface between two drops of clean mercury is zero, and they unite to form one drop. Many dissimilar liquids, on the other hand, which have very different surface tensions, will also diffuse into each other and mix in all proportions.

Marangoni states that in all cases in which liquids do not mix, that possessing the smallest surface tension will spread over the one which has the greatest. At one time water and mercury were supposed to be exceptions, but it has been shown that water will readily spread over a mercury surface, if the latter be chemically clean. This subject has engaged the attention of Lord Rayleigh,[1] who concludes that the interfacial tension between any two bodies is proportional to the square of the difference of certain values, peculiar to them, analogous to density in the theory of gravitation.
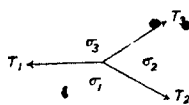
Fig. 12.

Thus, suppose we have three fluids, the interfaces of which meet along a line perpendicular to the paper (see fig. 12). Making T_1, T_2, and T_3 the interfacial tensions, and denoting the property analogous to density by σ_1, σ_2, and σ_3, then, according to Lord Rayleigh,

$$T_1 \propto (\sigma_3 - \sigma_1)^2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$
$$T_2 \propto (\sigma_2 - \sigma_1)^2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$
$$T_3 \propto (\sigma_3 - \sigma_2)^2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

It will be found that whatever the three respective values of σ in the above expressions, the interfacial tension T_1 between the liquids of greatest and least 'density' will always exceed the combined tensions T_2 and T_3 of the other interfaces, and that, consequently, the liquid of intermediate tension will always be drawn in between those of greatest and least surface tension.

This theory has an important bearing upon diffusion phenomena, for when two miscible liquids are brought into contact the interface immediately disappears, and there is substituted for it a thick layer,

[1] "Theory of Surface Forces," *Phil. Mag.*, Dec. 1890, p. 463.

across which the value σ changes gradually from that of one liquid to that of the other. According to this, the whole force due to the surface tension of any two miscible liquids in contact may be considered as distributed over the space in which diffusion is taking place, and, as the number of contiguous layers may be regarded as infinite, the force between each layer becomes infinitely small, and it has been shown that the sum of the forces must be zero.

Surface Tension of Solids.—It was not until the surface tension phenomena of solids were recognized that the theory assumed its present form, for it will at once be seen that the above applies to the surface molecules of solids as well as liquids, and also to the molecules at the bounding surfaces of solids and liquids, even when in contact with gases.

In solids, as in liquids, the molecules attract each other powerfully, and the surface molecules are in the peculiar condition of having the stresses arranged differently in directions parallel to and normal to the surfaces. The surfaces of solids must, therefore, be in a state of tension ; but, in their case, the stresses are not sufficiently powerful to produce readily perceptible deformation of the mass. Very viscous liquids, such as pitch, do show the reality of the stress, even when the liquids are so viscous that they act very much as solids do ; for, in the course of time, they round off their sharp corners and show all the peculiar surface tension phenomena of mobile liquids. A piece of glass, having sharp cutting edges, when heated rounds off its corners. It would scarcely be logical to argue that superficial tension only comes into existence the moment the solid is softened by the heat. Rather must we consider that the surface was in a condition of stress before the glass was heated, but that the tension only showed itself when the mass ceased to be rigid.

Beilby,[1] by microscopical methods, has demonstrated the existence of surface tension in solids. He found that when a surface of even such a brittle substance as speculum metal was rubbed with fine emery cloth, the ridges and grooves so formed all had rounded edges, and that by polishing with leather the material forming the ridges was easily caused to flow into the hollows, producing an optically good surface. From the manner in which liquids spread over solid surfaces it is clear that the surface tensions of the former are much less than those of the latter. Taking a surface film of water as having a thickness of six millionths of a millimetre and a tension of 73 dynes per centimetre, the stress of such a water film amounts to about 0.8 ton per square inch. It is probable that in the case of a solid the tension is so great that the surface is caused to flow at all edges and corners, and that therefore, as Beilby found, an edge comparable with molecular dimensions is an impossibility.

Contact between Liquids and Solids.—The behaviour of liquids and gases in contact with solids is really in accordance with theory. A particular liquid does not, for instance, act towards all solids in the

[1] "The Surface Structure of Solids," *Jour. Soc. Chem. Ind.*, 1903, 1166.

same way. Water will wet and spread over a clean sheet of glass, but when a drop of water is placed upon a sheet of solid paraffin wax it draws itself up into a bead. Mercury will not wet any known solid with which it does not amalgamate. From this we conclude that mercury has a greater surface tension than glass, and that water has a surface tension greater than that of paraffin wax, but less than that of glass. All lubricants have surface tensions much smaller than those of the metallic surfaces to which they are applied : they consequently spread over them and wet them.

Although, according to Marangoni and Laplace, three fluids cannot rest in contact, yet if two liquids and a solid be brought together, the latter being a body of intermediate surface tension, neither of the liquids can spread completely over the solid, for the tension at the interface between the solid and any one of the liquids can never exceed that at the other two.

Fig. 13 illustrates this. Here the solid σ_2 has a flat surface, and
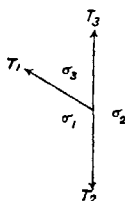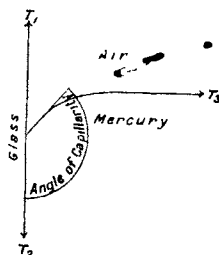
FIG. 13.   FIG. 14.

against it rest the liquids σ_1 and σ_3, the former having a smaller and the latter a greater tension than that of the solid. So long as the magnitudes of the surface tensions are thus distributed, then T_1 (the interfacial tension between the liquids of greatest and least 'density') is greater than the sum of T_2 and T_3, and the point of meeting is drawn along the surface of the solid until T_1 assumes such an angle with the solid surface that the forces are in equilibrium. It will be noticed that the tension T_1 is tending to wrinkle the solid surface and draw it between the two liquids, so as to arrange the three bodies in the order of their surface tensions.

When a liquid of high surface tension, such as mercury, is resting upon a solid of lower surface tension, such as glass, although the liquid does not spread over the solid and wet it, there is really a close union of the two masses, which can only be parted by the exercise of force or the interposition of a liquid of intermediate surface tension. Indeed, so close is the contact of mercury and glass that the vacuum in a barometer remains unaffected for years.

Fig. 14 illustrates the conditions obtaining in a tube immersed in

mercury. Here T_2 is so much more powerful than T_1 that the mercury surface is depressed until T_3 makes such an angle with the surface of the solid that T_1 and T_3 together balance T_2.

When oils and water are brought into contact with metals, the liquid of least surface tension is not of necessity easily displaced by the liquid having the greatest surface tension, for everything depends upon which liquid touches the metal first. Thus, if the metal be made perfectly clean, and then dipped into oil, water cannot penetrate between the solid and the lubricant, for the metallic surface has become so contaminated by the oil that it behaves as though it were a solid surface of smaller surface tension than water. On the other hand, if the clean metal be first wetted with water, the oil, being the liquid of least surface tension, cannot displace the water, unless aided by mechanical action. This reasoning accords well with what is known concerning the action of water in steam cylinders, for when copious condensation takes place, and the water cannot get away freely, efficient lubrication is almost an impossibility. This, of course, does not apply to cloudy steam impinging upon rubbing surfaces. In such a case each minute drop of water may be covered by a pellicle of the lubricant, which necessarily reaches the metallic surface first and lubricates it.

The readiness, however, with which solid surfaces become contaminated by many substances, and the difficulty experienced in cleaning them again, is satisfactorily explained by assuming that the surface molecules exert a very considerable attractive force on surrounding matter. Indeed, freshly formed solid surfaces at once attach to themselves from the air an exceedingly thin coating of moisture, which is in a few hours replaced or supplemented by a layer of grease. Such contamination films are probably not always continuous sheets covering the surfaces and separated by an abrupt line of demarcation from the solid, but mixtures of liquid or gaseous molecules with the surface molecules of the solid.

Although Lord Rayleigh's theory concerning the comparative intensities of the surface tensions of liquids and solids serves to explain very clearly some of the most striking surface tension phenomena, it must not, as he says, be followed too far ; for there still remain numerous phenomena which it fails to explain, or is even in apparent conflict with. However, even if the hypothesis is too narrow to accord with all the facts, it illustrates clearly the main points with which we have to deal.

Circumstances which modify Surface Tension.—*Temperature.*— If a thin film of oil be spread over the upper surface of a metal plate, and a hot iron be caused to touch the underside, the oil will shrink away from the heated spot and leave it almost clean. This is caused by a decrease in the tension of the heated oil surface, and the consequent drawing away of the oil by the cooler surrounding film.

It appears that with rise of temperature the surface film tensions of all liquids diminish, and less energy is required to separate their

molecules. Thus, in converting water into steam at $212°$ F. $965\cdot7$ units of heat per lb. are required, whereas at $371°$ F. $649\cdot0$ suffice.

Owing to this reduction of surface tension by heat, the oil film on a heated bearing is drawn away from the rubbing surfaces by the greater superficial tension of the film on the surrounding cool parts, and the lubrication becomes more and more defective as the bearing gets hotter, owing to the creeping away of the oil, as well as to its lessened viscosity.

Solubility.—We have hitherto referred to the contact surfaces of dissimilar liquids, gases, and solids as though they really were sharp surfaces of demarcation between the opposing molecules of the media in contact. Such, however, is not the case, for many liquids are *partially*, if not wholly, soluble in each other. Ether, for instance, dissolves in water, but when more than one part of ether is added to ten parts of water the excess of ether remains separate from and insoluble in the aqueous liquid. Similarly, ether dissolves about three per cent. of water. The interfacial surface between mixtures of these liquids does not, therefore, separate ether from water, but rather abruptly separates mixtures of the two liquids from each other.

Contamination of Liquid Surfaces.— Lord Rayleigh[1] and Miss Agnes Pockels[1] have shown the remarkable effects that even traces of foreign substances exert upon the surface tension of water. It is, in some measure, this marked action of traces of impurity which makes experimental work on surface tension phenomena so difficult and which places such obstacles in the way of the practical application of our present knowledge. Miss Pockels used a rectangular trough 70 cm. long, 5 cm. wide, and 2 cm. deep, filled with water to the brim. A strip of tin, about $1\frac{1}{2}$ cm. wide, was laid across it at right angles to its length, so that the underside of the strip was in contact with the surface of the water and divided it into two portions. By moving this partition, the surface area could be varied to any desired degree. The surface tension was measured by the force necessary to separate a small disc from the surface. A perfectly clean surface was obtained by placing the tin partition at one end of the trough and drawing it across the surface, thereby sweeping off the contamination. Such a surface retains an approximately uniform contractile force, however much the partition may be moved and the area varied. Or the other hand, a *strongly* contaminated surface was found to have a variable surface tension.

The effects of contamination films may be shown by sprinkling upon a *clean* surface of water lycopodium grains or other suitable powder. The water surface, if touched by a needle which has been dipped in oil, will at once become contaminated, and the effect produced by the spreading of the oil over the surface is as though a hole had been pricked in the film, for the dust-covered surface draws rapidly away from the oiled centre and crowds the dust particles towards the edge of the vessel. A drop of alcohol allowed

[1] *Nature,* vol. xliv. (1891), p. 437.

to closely approach or touch the water surface weakens the tension of the film in a similar manner.

To show how greatly the surface tension of water is altered by a trace of oil, a light rubber ring may be floated upon a clean water surface. The tensions of the surface film being the same inside and outside, the ring, by its elasticity, assumes a circular form. On bringing a little oil into contact with that portion of the water surface outside the ring, the surface tension is diminished, and the superior tension of the internal film then distorts the ring or even causes it to collapse completely.

Solvent Power of Surface Films.—There is reason to believe that the solubility of liquids, and also of gases in liquids, follows different laws in surface films, where the molecules are in peculiar conditions of strain, than it does in the interior of liquids.

This may be shown in many ways. For instance, a thin disc of camphor so placed that it is half immersed in clean water will, in the course of a few hours, be cut through by the superior solvent action of the surface film. In some cases the action is reversed, and the mass of the liquid displays a greater solvent power than the surface layer.

The superior solvent power of a water film over the mass of the liquid has been shown by Dupré and Rayleigh, who found that, at the first moment of their formation, surfaces of soapy water have hardly less tension than pure water, but that the molecules of the dissolved soap gradually collect in the film and greatly modify its properties.

This concentration of the dissolved substance in the surface film also takes place when the interface is one separating a solid from a liquid, for it has long been known that vinegar can be partially deprived of its acid by filtration through pure quartz sand.[1] Potato spirit, if filtered through clean sand, passes water first, then alcohol, and finally alcohol plus fusel oil.

Gore[2] made a number of interesting experiments on the behaviour of various aqueous solutions in contact with finely divided silica. He found that, on agitating dilute solutions of acids, alkalies, and salts with this powder, and allowing it to subside, the solid in many cases abstracted as much as 80 per cent. of the dissolved compound.

This concentration of a dissolved substance on the contact surface of the liquid with the solid enables a lubricant to be applied with ease, and without serious waste, to the friction surfaces of hydraulic machinery. The more or less soluble lubricant, usually soft soap, is added to the water before it enters the pipes, and then, by concentrating upon the rubbing surfaces, lubricates them and greatly reduces the friction and wear.

Surface Energy.—*Proportional to Surface Area.*—As any increase in the area of a surface involves the expenditure of work, and as

[1] Gmelin's *Handbook of Chemistry*, vol. i. p. 114.
[2] *Chem. News*, vol. lxix. p. 22.

either increase or decrease in the value of the tension of a surface produced by its closing upon another surface, or coming into contact with a contaminating substance, alters the work such a surface is capable of doing, each unit of area of such surface represents so much available energy. Indeed it acts like a stretched sheet of rubber, which can do work by contracting. We must, therefore, regard the total energy of a body as not being solely due to its temperature and its volume, but as also depending to a certain extent upon the area of its surface.

The separation of a drop of any liquid into two or more parts can only be accomplished by the expenditure of work, for the volume of a sphere is proportional to the cube of its radius, whereas its superficial area is only proportional to the square of the radius. Thus, the finer the state of division of the liquid, the greater the superficial area in proportion to the volume. The total energy of a liquid is therefore increased by breaking it up into separate drops, and the total energy of the mass must include this energy as well as that due to its temperature and volume. A given weight of steam, which is water broken up into separate molecules, has therefore more potential energy than the same weight of water in its liquid state and at the same temperature.

Emulsions.—Emulsions are generally composed of gelatinous or oily liquids suspended in the form of exceedingly small drops in other liquids into which they neither diffuse nor dissolve. Generally speaking, the individual globules may be clearly distinguished under the microscope, as in the case of milk. In some instances, each liquid particle is surrounded by a film separating it from the liquid in which it floats.

In other cases, when emulsification takes place, the liquid forming the matrix has had its surface tension so altered by the introduction of a third substance, or is naturally of such a nature, that its film resists rupture and prevents the coalescence of the drops of oil.

Cause of Wetting.—Gore showed that when finely divided silica is introduced into water, or into an aqueous solution of any salt, a rise of temperature results. In this experiment, a surface between air and silica is exchanged for one between the liquid and silica. As water spreads over silica and wets it, the surface tension of silica must be greater than that of water, and that of the interface between these must have some intermediate value; consequently, when the water replaces air, a liberation of energy takes place and the temperature rises. Other effects, resulting in a liberation of heat, may of course be produced as well.

We thus see that the reason why lubricants may be spread over solids and caused to *wet* the whole of their surfaces is that the liquids have lower superficial tensions than the solids, and the *wet* condition is the one of least potential energy.

A clean glass rod dipped into mercury, water, and oil gives very different results. The relative surface tensions of the liquid and solid are not such as to enable the mercury to adhere to the

glass permanently. As pointed out previously, the mercury and glass do adhere, but the mercury is drawn off by its weight and strength of film. It is otherwise with water, the smaller superficial tension of which causes it to spread over the glass, which remains wetted when removed from the liquid. When the dry glass rod is immersed in oil and is then removed, the oil, like the water, remains on the glass, but as a thick instead of a thin film. The reason why a larger volume of oil than of water adheres to the rod is that the viscosity of water is small, whereas the oil is very viscous and flows much more slowly. Sufficient time being allowed, both oil and water run off and leave very thin films on the glass.

Capillarity. — *Capillary Rise in Tubes.* — Although this is merely a striking manifestation of superficial tension, it is commonly known as 'capillary attraction,' having in the first instance been studied in connection with capillary tubes.

When experimenting on capillary phenomena, care should be taken that all the tubes, etc., employed are quite clean. If the surfaces be chemically clean, and the liquid experimented on possesses a smaller superficial tension than the solid, the liquid will at the moment of contact with the solid rise and wet the whole of its surface. As, however, a clean tube may quickly become soiled, it is better, after cleaning the tube, to at once moisten it all over with the liquid to be experimented on, and thus to ensure that the effects shall not be interfered with by atmospheric impurities.

When a tube which has thus been cleaned and moistened is dipped into a beaker of water, the liquid rises rapidly in the bore and may reach a height of an inch or more. When this takes place in a moist atmosphere, the whole of the surface of the tube, both internally and externally, is covered by a film of water which is continuous with the water in the beaker. On the outside of the tube the vertical stress of the film raises a small ring-shaped mass of water above the general surface level, the weight of which just balances the tension of the film. On the inside of the tube the tension of the film covering the walls of the bore draws up a long column of water, which also balances the tension of the internal surface film and is a measure of its pull. Hence, the height to which the liquid is drawn up in the tube varies inversely as the radius of its bore.

But in order to secure the rise of a liquid column above the general surface, it is by no means essential that a tube should be used. A few parallel lengths of wire held so as to enclose a small space will also produce the same effect.

Fig. 15 is an enlarged section of four parallel wires which dip vertically into the liquid. Between these wires superficial tension surfaces form, and furnish walls which act much as the walls of a rubber tube would, converting the bundle of wires into a tube up which the liquid rises.

Flow through Wicks. — A worsted thread or a lamp wick is really a similar contrivance, and, as the strands are very fine and close

together, the liquid often rises several inches. So long as the surface
tension of the fluid is less than that of the material of which the wick
is made, and therefore wets it all over, the liquid column rises to a
height proportional to the surface tension of the fluid. When such
a partly immersed wick hangs down outside the vessel containing
the liquid, if the lip of the vessel be not too high, then the wick
constitutes practically a number of small siphons, through which the
fluid flows. In such capillary passages the flow is steady, and
the volume passed is directly proportional to the head and inversely
proportional to the length of the wick and the viscosity of the fluid.

Fig. 16 shows such a case. Here the height h of the column
producing the flow is measured from the surface of the vessel to the
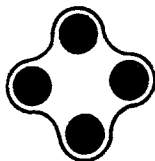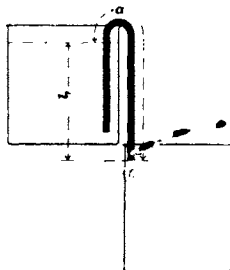
FIG. 15.   FIG. 16.

end of the wick, whilst the length a of the wick gives the length of
the capillary passages.

From Poiseuille's formula for the flow of liquids through capillary
tubes (see p. 22) we find that the volume passed in t seconds is

$$V = C \frac{g\rho h t}{\eta a}$$

the value of C varying with changes in the size and texture of the
wick.

It must be remembered that in the case of siphon wicks the walls
of the passages along which the liquid flows, consist partly of liquid
surfaces. Consequently, as soon as the suction at the top of the
siphon becomes too great for the surface tension to balance it,
owing to the fall of the surface in the reservoir, the liquid walls
collapse, air is drawn between the strands, and siphoning ceases rather
suddenly. On this account, the above formula does not hold if the
long 'leg' of the wick should fall so low that the weight of liquid
in it can of itself distort and rupture the external film. Strands of
worsted consist of rather coarse fibres, and cannot be depended upon
to raise the liquid over a lip rising about $1\frac{1}{4}$ inches above the liquid

surface. When more powerful lifting action is required, as in lamp wicks and the strands used to supply lubricants to railway axle pads, cotton pleated very finely is used instead of worsted.

All such wicks, pads, strands of worsted, etc., when exposed to the air, absorb moisture and other substances. Oil will not, therefore, flow freely through them until they have been well dried and then wetted with the liquid in which they are to work. The volume of lubricant such wicks will supply depends, as we have seen, not only upon the superficial tension or capillarity of the liquid, but also upon its viscosity. The height to which it rises increases with the superficial tension and the fineness of the external mesh of the wick.

Measurement of Surface Tension — *The Force to be Measured.* — We have seen that the surfaces separating solid, liquid, and gaseous substances from each other are in a state of tension, and that the magnitude of this tension varies with the nature of the substance or substances in contact, or, when the surfaces are not clean, with the nature and extent of the contamination. Such surfaces act like stretched sheets of indiarubber, but the tension is always the same in all directions, and when not contaminated, has the same value however much the film may be extended.

In fig. 17, let ABCD be a stiff wire frame upon which the cross wire PQ slides freely. In the area enclosed by the wire is a liquid film, a measure of the tension of which is required. This film, it will be remembered, consists
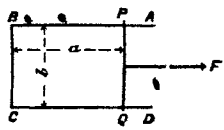
FIG. 17.

of two tension surfaces which pass round and grasp the wire frame and slider on all sides. The two surfaces are separated from each other and from the surface in contact with the wire by an inactive liquid layer of variable thickness. The active liquid surface layer which produces the tension effects has a thickness of about six millionths of a millimetre ; the water layer enclosed may be a hundred or more times thicker than this. To prevent the elasticity of the film from drawing the cross wire PQ towards BC, a force F must be maintained, acting in the direction of the arrow. If T be the superficial tension and b the distance apart of the wires BA and CD, then, as there are two surfaces to the film, separated by liquid,

$$F = 2Tb.$$

Capillary Tube Method - -The method which has usually been adopted for measuring the superficial tension of liquids is by ascertaining the height to which they rise in capillary tubes. The degree of accuracy obtainable is limited by (a) the narrowness of the tube, (b) irregularities in the bore, (c) the shortness of the elevated liquid column, (d) the difficulty of measuring the mean height of the liquid, and (e) the difficulty of securing a clean surface. The method is quite accurate enough, however, for all practical purposes.

Fig. 18 shows the conditions of equilibrium of a liquid which has a smaller tension than that of the material of which the tube is made. A film of the liquid is drawn over the whole of the surface of the bore, and by its tension the liquid is drawn up until it just balances the weight of the

column. A very simple calculation gives the superficial tension of the liquid. If r_0 be the radius of the tube, ρ the density of the liquid, g the force of gravity, and h the mean height attained in the capillary tube, the vertical force (W) $\qquad = 2\pi r_0 T$ . . . . . (6)

This supports a weight of liquid $(W) = \pi r_0^2 h \rho g$ . . . . . (7)

Consequently, $2\pi r_0 T = \pi r_0^2 h \rho g$ (8); and $T = \dfrac{r_0 h \rho g}{2}$ . . . (9)

This method only holds true when the liquid has a smaller superficial tension than the solid, and spreads over it. But there are cases, such as mercury in contact with glass, where the liquid has in all probability a greater surface tension than the solid. In such an instance, although the liquid adheres with some force to the solid, it cannot spread over it, and the solid on account of its rigidity cannot spread over the liquid; consequently, the combined effects of three
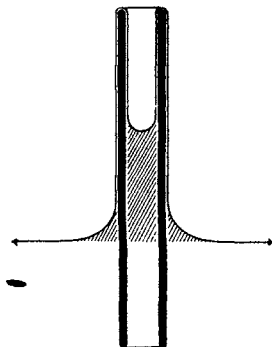
Fig. 18.
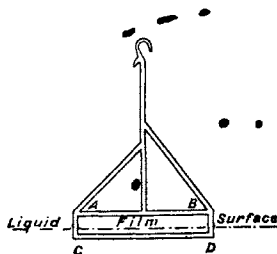
Fig. 19.

tensions have to be dealt with, as shown in fig. 14. The vertical component in this case may act downwards, and the tension of the surface of the meniscus where it touches the glass acts at an angle. But no known lubricants have greater superficial tensions than has glass, and consequently, although such cases are interesting to physical students, they have little if any practical importance.

Measurement by Film Tension.—A direct method of measuring the strength of the tension has been employed by Proctor Hall[1] at the suggestion of Prof. Michelson.

A glass frame, fig. 19, is suspended from one arm of a delicate balance, so that it is partly immersed in the liquid. The weight is first taken when a film of the liquid is extended between the bar AB and the liquid. The lower bar is completely submerged, and serves merely to stiffen the end portions which dip into the liquid. After breaking the film another reading is made, care being taken that the frame

[1] *Phil. Mag.*, Nov. 1893.

remains immersed in the liquid to exactly the same depth as before. Such a film consists of two surfaces which have closed together and looped round the bars of the frame. The surface tension is the difference between the two weighings, divided by twice the width of the frame. When *very* exact determinations are required, a small correction has to be made for the width of the frame, as the film distorts the capillary rise of the liquid on the inside of the vertical bars AC, BD. The amount of this correction is found by taking the tension of the same liquid with two or more frames of the same thickness, but of different widths.

Fig. 20 shows in section the conditions when there is a film in the frame. The tension that may exist on the face separating the liquid from the frame has no effect whatever on the balance, for the surface where the air and the liquid meet encloses the upper bar and closes together to form a film beneath it. This film it is which supports the mass of liquid which is shaded in the figure and which acts upon the balance.

Measurement by Wetted Plate.--The films of some liquids, such as alcohol, ether, and chloroform, break almost immediately they are
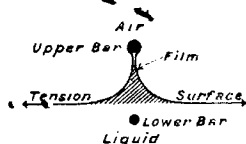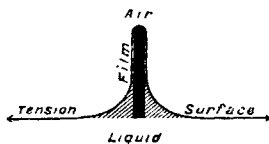
Fig. 20.   Fig. 21.

formed, consequently their superficial tensions cannot be found by this method. Proctor Hall, therefore, adopted a modification of Wilhelmey's method. The glass or metal frame was replaced by a thin rectangular plate of glass, mica, or metal. The plate was adjusted by trial over a liquid until the whole edge seemed to enter the liquid at once when lowered into it, and when raised slowly parted from the liquid, first at both ends and lastly at the middle of the lower edge.

Fig. 21 shows in section the conditions obtaining. The tension surface, separating the air and the liquid, rises over the solid and envelops it, and by its contractile force draws up the two shaded masses of water, the weight of which the balance measures. The results are obtained as follows:— The index of the balance is brought to zero. The vessel containing the liquid is then slowly raised until the liquid touches the under edge of the plate and wets it. As soon as this takes place, the liquid film spreads over the plate and by its tension acts on the balance. The balance is again adjusted to zero, and the lower edge of the plate is thereby also brought to its original level. Where b is the breath, τ the thickness of the plate, and T the surface tension

$$W = 2(b + \tau) f \qquad . \qquad . \qquad . \qquad . \qquad . \quad (10)$$

Both these methods have been found to give concordant results and to admit of extremely accurate work with some liquids; but Richardson and

Hanson have found them unsatisfactory for mineral lubricating oil, and have obtained better results by the capillary tube method.[1]

Instead of a plate, a vertical tube may be slung from a specific gravity balance, the vessel containing the liquid resting upon a table which can be raised and lowered by a rack. Making W the weight on the balance, r_1 the inside and r_2 the outside radius of the tube, then

$$W = T(2\pi r_1 + 2\pi r_2) \quad . \quad . \quad . \quad . \quad . \quad (11$$

$$\text{and } T = \frac{W}{2\pi r_1 + 2\pi r_2} \quad . \quad . \quad . \quad . \quad (12$$

In other words, the weight divided by the inside circumference plus the outside circumference gives the surface tension.

For a description of this and other methods of measuring superficial tension the paper by Proctor Hall [2] should be consulted.

In all cases, the surface tension of the liquid to be measured must be less than that of the solid plate or frame, or the former will not spread over the latter and form a film acting in a direction parallel with the solid surface. A little grease or oil on the plate will so reduce the superficial tension of the solid that water will not spread over it. In all cases, the solid should be well washed with caustic soda solution, well rinsed in clean water, and then heated in a Bunsen flame.

Cohesion Figures.—Although in the practical testing of oils the observation of the curious forms assumed by the spreading of oil drops on clean water surfaces has not yet been found to be of much practical value, cohesion figures are of great interest, and may yet be found of service.

When a drop of oil is allowed to fall on water, although it quickly contaminates the whole of the water surface, the greater portion remains as a lenticular mass, which spreads with greater or less rapidity, becomes perforated with holes, forms beautiful lacelike figures, and finally separates into numerous lenticular discs. Different oils produce in most cases different figures, and these figures are altered by the presence of adulterants. The thickness of the contamination film surrounding the oil discs is exceedingly small—about two millionths of a millimetre—and the tension of this attenuated film would seem to be about as great as that of the combined pull of the oil-air and oil-water surfaces enclosing the lenticular masses of superfluous oil. This tendency of the two surfaces of a film to close together and force the excess of fluid to collect in separate masses resembles closely the phenomena observed in soap bubbles by Reinold and Rücker, who noticed that the thin black film was often surrounded by one having a thickness 250 times as great.

It is clear, however, that before the significance of the action of the surface forces of liquids and solids upon some of the more obscure phenomena of lubrication can be satisfactorily ascertained, further research upon surface tension phenomena will be required.

[1] *Jour. Soc. Chem. Ind.*, xxiv. (1905), 315.   [2] *Phil. Mag.*, Nov. 1893.

CHAPTER IV.

Lubrication and Friction.—*Lubrication of Surfaces.*—In Chapter I. the subject of solid friction was dealt with in detail, and it was pointed out that unless solid surfaces be contaminated by lubricating substances they generally seize and abrade each other, even under very small loads. Such contaminated surfaces cannot properly be called lubricated surfaces, for the particles of the lubricant are merely entangled in the minor surface irregularities of the solid, while still leaving it rough. The laws of solid friction appear to be unaffected by the presence of contamination films, which only serve to reduce the coefficient of friction and enable metals which would otherwise seize to work together at moderate pressures.

On the other hand, when a surface is properly lubricated it is flooded with the viscous or plastic lubricant, and the coefficient of friction depends chiefly upon the nature of this lubricant and the form of the surfaces. At high speeds, and often at comparatively low speeds also, such well lubricated surfaces are wholly separated from each other, and the friction then depends upon the thickness of the lubricating film, the area of the surfaces in contact, their relative velocities, and the viscosity of the lubricant.

Although the difference between a contaminated and a lubricated surface is only one of degree, it is convenient to consider surfaces which have been wiped clean as contaminated, and surfaces which are *wet* with the lubricants as lubricated.

Objects of Lubrication.—In the design of machinery, the engineer seldom has to deal with unlubricated rubbing surfaces. His object is the transference of energy, and its utilization at some particular place, with as little loss as possible. In effecting this, the relatively moving surfaces are often pressed together with considerable force and caused to slide over each other at high velocities. Unless such surfaces be kept apart by the interposition of a lubricant, the frictional losses will be great, and the wear and tear of the surfaces, in most instances, proportionately serious. Indeed, were it not for the properties certain liquids and soft solids possess of keeping the

48

relatively moving surfaces apart, and thereby reducing the frictional resistances between them, it would be impossible to carry on many most important manufacturing processes, or to move vehicles at anything like railway speed.

Frictional Losses.—It has been estimated [1] that the total horse-power of all the steam engines at work in the United Kingdom at the present time is not less than ten millions, and that consider-ably more than half this enormous amount is consumed in over-coming friction.   Prof. Charnock says: "It is truly remarkable that of the many details in connection with machinery, none receives less attention than the reduction of friction and the proper lubrication of bearings.   With a constant striving after the reduction of steam consumption per indicated horse-power, little thought is bestowed on the relation of indicated horse-power to the useful work done.   Taking a good engine working at full power, from 6 to 8 per cent., and at quarter power from 24 to 32 per cent., of the total power developed, is wasted in friction of the main bearings.   In many mills fitted with first-class arrangements for transmitting power, to drive the shafting alone requires from 20 to 30 per cent. of the useful work done by the engine, and no doubt in many cases this is greatly exceeded.   Very little indeed is known of the power required to overcome the friction of various classes of machinery used in mills and factories, but it is safe to say that the work usefully expended in the actual operations which the machinery is intended to perform must be an exceedingly minute fraction of the power developed by the steam engine in the first place.   It is evident that there is much room for progress in the direction of the reduction of avoid-able sources of loss by more careful attention to the laws of friction, and to more scientific methods of lubrication."

In this connection Prof. J. Goodman [2] has also remarked that "out of every ton of fuel consumed for engine purposes, some 400 to 800 lbs. are wasted in overcoming the friction of the working parts of the motor, and further, every machine driven by a motor also wastes a large percentage of the remaining power by its own friction.   One would not be far short of the mark in saying that from 40 to 80 per cent. of the fuel is consumed in overcoming friction.   This extremely wasteful state of affairs is most unsatis-factory, and happily can be greatly improved by a due observance of the laws of friction and lubrication."

The full benefit derivable from efficient lubrication could seldom be taken advantage of until recently, for bearings as formerly con-structed could not be perfectly lubricated without involving a great waste of oil.   But now that the mechanical problems to be solved have become better known, such defects can be, and have been to a great extent, remedied in modern machines

[1] Lectures given before the Bradford Engineering Society by Prof. G. F. Charnock, Nov. and Dec. 1905, p. 1.
[2] Paper read before the Manchester Association of Engineers, March 1890.

Theory of Lubrication.—Until recently, the engineer had to be guided almost wholly by experience in the design of bearing surfaces and the methods of their lubrication; the theory of lubrication, or of the action of viscous or plastic substances in diminishing friction between relatively moving solids, having received little attention. Not that experimental investigations had been neglected; as a matter of fact a vast amount of experimental data had been collected, but the results not only failed to agree with each other, but they also failed to agree with the general experience of engineers concerning the frictional resistances of machinery. The experiments of Beauchamp Tower, however, undertaken at the instance of the Institution of Mechanical Engineers,[1] have helped to explain the reason of most of these discrepancies. He proved that a great deal depends upon the way in which the lubricant is applied to the bearing, the friction varying with the quantity and uniformity of distribution of the oil, as well as with the form of the bearing, the speed, etc. Most of his recorded experiments were made in such a manner that the lubrication was 'perfect'; *i.e.* the bearing was flooded with oil. The results were comparable with each other, agreed better than previous experiments with the frictional resistances met with in such complex machines as steam engines, and were in close agreement with hydro-dynamical theory. Taken in connection with other experimental results, they have, thanks mainly to the work of Osborne Reynolds, enabled us to frame a fairly complete theory of high speed lubrication.

Unfortunately, the same cannot be said of our knowledge of the static or low speed friction of lubricated surfaces. On this subject we can only point out those conditions which seem to be of importance, and give such experimental data as are available.

The theory of high speed lubrication is based upon the supposition that a lubricant acts in virtue of its viscosity and density, physical properties which cause the fluid lubricant to insinuate itself between the relatively moving surfaces and force them apart. Such lubricants, however, offer considerable resistance to shear, and at high speeds it is this resistance which mainly occasions the friction of the bearing. The value of this resistance depends upon the viscosity of the lubricant, the relative speed of the surfaces, their area and inclination to each other, and also upon the thickness of the lubricating film at each point. When these conditions are known, the resistance offered to their relative motion can, very approximately, be calculated. That these really are the conditions which determine the friction will be seen when we come to consider bearings of different kinds and compare the experimental results with those deduced from theory.

Division of the Subject.—Bearing surfaces are of various shapes, the most common form being cylindrical; often, however, they are true planes; but whether cylindrical or flat, the opposing surfaces,

[1] *Proc. Inst. Mech. Eng.*, 1883, 1885, 1888, 1891.

when working, are seldom quite parallel to each other.   In discussing
the theory of lubrication, the subject will be treated under the
following heads :—

               1. Static Lubrication.
               2. Low Speed Lubrication.
               3. High Speed Lubrication.

This order of treatment is convenient, as, although at high speeds
the friction depends very greatly upon the shape of the surfaces and
the free supply of the lubricant, such is not the case at low speeds,
for the surfaces then act as though they were approximately parallel,
and the lubricating films very thin in places.

Static Lubrication.—*Influence of the Thickness of Lubricating
Films.*—When two surfaces between which there is a viscous lubri-
cating fluid are pressed firmly together, the lubricant is slowly
expelled, the faces eventually approach one another very closely, and
in order to cause them to commence sliding over each other, con-
siderable force has sometimes to be exerted.   It is evident that if the
solid surfaces were perfectly smooth, and the film had an appreciable
thickness, any force, however small, would cause relative motion ; for,
in the case of a viscous fluid film (see p. 18 (5)),

$$F = \eta \frac{v_1 a^b}{r_0} \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

the resistance F being proportional to the speed v_1, so that when
$v_1 = 0$, $F = 0$.

But bearing surfaces never are perfectly smooth, and, as in the
case of so-called solid friction, the projecting particles interlock
somewhat, even though they may be prevented from actually touch-
ing each other by the presence of the intervening lubricant.   It is to
this *interlocking* that the static friction must be mainly attributed ;
consequently, the extent to which the film of any particular liquid
can be reduced in thickness by the pressure urging the faces together
is a very important consideration.

Static Coefficient of Friction.—Our knowledge of the static coefficient
of friction of well lubricated surfaces is by no means complete.   Thurs-
ton,[1] however, has described some experiments which he considers, on
the whole, to have been reliable.   He found that with different oils
the variation undergone by the static coefficient with increasing load
is very similar for each liquid, although the value of their frictional
resistances may differ considerably.

Fig. 22 exhibits graphically the results obtained by Thurston with
his oil-testing machine, when sperm oil and lard oil were used.   With
sperm oil (A) the static coefficient rose very rapidly until a pressure
of about 70 lbs. per square inch was reached.   It then increased less
rapidly to 500 lbs., and more rapidly again to 750 lbs., whilst at the

          [1] *Friction and Lost Work*, p. 315.

last observation, 1000 lbs., a further falling off was experienced. Lard oil (B), although having about twice the viscosity of sperm oil, gave a much lower coefficient of friction, but it behaved similarly, the
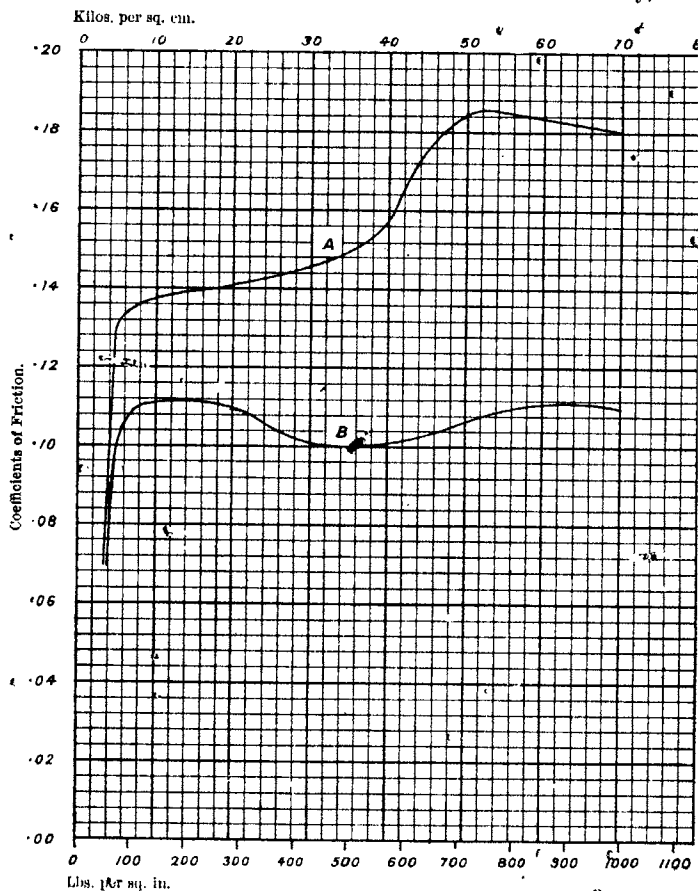
FIG. 22.

coefficient rapidly rising with increase of load up to 100 lbs. per square inch. Above this load, however, it decreased, passing the maximum at about 150 lbs., reaching the minimum at 500 lbs., and rising to a second maximum at 900 lbs. The general character of the curve is the same as that for sperm oil, but with the terminal portion

depressed. Heavy lubricating petroleum behaved very much like sperm oil.

Lard oil must, therefore, remain, in spite of the load on the bearing, as a much thicker film between the surfaces than sperm oil, and must keep the irregularities from interlocking to a greater extent. Here the smaller coefficient of friction is given by the liquid having the greater viscosity. The higher pressures stated are much greater than it has been found possible to employ in practice when the load is not intermittent.

Plastic Friction.—When the lubricating film is a plastic substance, such as axle-grease, the conditions are different, for such a film cannot be wholly expelled by pressure, and under ordinary working conditions may remain so thick that the metallic surfaces never actually touch, nor do the projections interlock.

That the film cannot be wholly expelled will be seen from fig. 10, p. 29. The two surfaces AB and CD are supposed to be approaching without tangential (sliding) motion, and the plastic lubricant is being expelled from between them by the pressure set up. The load urging the surfaces together remaining the same, the thickness of the film decreases until those portions of the lubricant the stresses upon which are sufficient to cause shear have been expelled. Further approach is then arrested.

Such a film offers, however, a measurable static resistance to shear. From experiments made with plastic lubricants (see p. 63) it would appear that under such loads as are used in practice, and when the surfaces are relatively at rest, the film is so thick that the static coefficient is much less than that given by even good viscous lubricants, and also that the coefficient of friction, when the speed is small, decreases steadily with decreasing speed until the static coefficient is approximated.

Effects of Superficial Tension.—Even when liquid lubricants alone are used, if the pressures forcing the surfaces together are not too great, the liquid film is only partially expelled, and the irregularities of metallic surfaces are, to some extent, prevented from interlocking and from cutting or abrading each other when set in motion. Different lubricants form films of very different degrees of thickness. The property does not seem to be in any direct way related to viscosity, for equally mobile liquids vary greatly in their power of forming thick stable films and reducing friction. Although this subject has been already dealt with at some length in Chapter III., we will again refer to a few of the main points which seem to have a bearing upon the static coefficient of friction.

Mineral, unlike animal and vegetable, oils, seem for the most part deficient in this property of forming thick, permanent films. When used for bearings which have to carry comparatively heavy loads on small rubbing surfaces, mineral lubricants are, therefore, often mixed with animal or vegetable oils, fats, grease, etc. The power which a liquid film possesses of resisting complete expulsion from between two

metallic surfaces may be regarded as due to two causes. ' In the first place, there is the interfacial action which causes oils to spread themselves over metallic surfaces. Rayleigh has shown that when several liquids are brought into contact with a solid whose surface tension is greater than that of either of them, the conditions of equilibrium or of minimum potential energy are satisfied when the liquid of greatest surface tension is in contact with the solid, and the other liquids assume the order of their relative surface tensions.

Water, however, although it has a greater surface tension, cannot, as a rule, displace oils, fats, greases, etc., from the surfaces of solids, for such substances are insoluble in water and insinuate themselves among the surface particles of the solid, from which they are not easily separated. When the temperature is high, and the surfaces abrade each other, water is apt to displace the lubricant and seriously increase the friction coefficient. Thus, water arising from condensation in steam pipes, etc., interferes seriously with the proper lubrication of valves, piston rings, etc., upon which it is apt to be deposited.

All lubricants have smaller surface tensions than the solids between which they are used, consequently they readily spread over and wet such surfaces. Were it not for this action, it would be impossible to apply the lubricant in many of the ways now commonly employed.

But in addition to this power of spreading over, or *wetting*, metallic surfaces, note must be taken of the power certain films possess of resisting *disruption*. For instance, a film of pure water ruptures almost immediately it forms. Such a film consists of two surfaces, in each of which the molecules are in a peculiar condition of stress. When the marginal molecules of the two surfaces meet, the film becomes locally weak and ruptures. The addition of a little soap, although it reduces the surface tension of the film by nearly one half, causes it to persist and strongly resist rupture at points where it has become thin.

Dupré and Rayleigh proved that, at the moment of their formation, surfaces of soapy water have hardly less surface tension than pure water. The soap in the film is slowly concentrated from the interior, and not only alters its tension and prevents it from rupturing, but also increases its viscosity. Clean water supplied to hydraulic machinery has little or no lubricating effect upon the bearing surfaces of valves and other moving parts, which, when unlubricated, abrade each other very rapidly. A little soap added to the water makes all the difference. The film *resists rupture*, feels 'soapy' between the fingers, becomes more viscous, and keeps the metallic surfaces from abrading each other. .

Owing to the concentration of the soap in the surface film, only a very small quantity is required to secure the proper lubrication of hydraulic valves, etc. '

The result produced by the varying thicknesses of the permanent greasy films of different lubricants has already been seen, as regards sperm oil and lard oil, in the case of the static friction coefficient. But as its value in lubricating problems is most marked when the speed is low and the loads high, detailed reference to it is convenient at this juncture.

Low Speed Lubrication.—*Influence of the Nature and Condition of the Friction Surfaces.*—At high speeds we shall find that with suitably designed bearings the lubricant becomes trapped in relatively considerable volume between the moving surfaces, and as it cannot escape freely again, the surfaces remain completely separated by a viscous film (see p. 64). At very low speeds, however, this is not the case, and if the load be too great, or the rubbing surfaces are of unsuitable materials, there is danger of so cutting and tearing the bearings that they will run hot. Static friction and low speed friction effects are, indeed, of great importance in almost all cases, for machines have generally to be started from rest with considerable loads on the bearings. This is especially the case with the axles of railway vehicles, the journals of which require very careful lubrication ; endurance and a low coefficient of friction being of paramount importance. The friction of turntable centres, of the motion pins of slowly moving engines, etc., and indeed of the rubbing surfaces of all kinds of slowly moving machinery, is largely dependent upon the nature of such surfaces, and upon the greasiness or oiliness of the lubricant used, its viscosity, and the rate at which the viscosity decreases with rise of temperature.

The irregularities of even smooth rubbing surfaces, although they may be separated over considerable areas by continuous films of the lubricant, often actually engage each other at numerous points. At such places abrasion occurs, often without serious results, for the liberated heat can, in most cases, pass freely away, and the lubricating film is not permanently broken. Should, however, the materials forming the bearing surfaces be such that when forced into contact, they readily weld together, large areas of the surfaces may eventually seize. Therefore, although at all ordinary running speeds the friction depends almost wholly upon the action of the lubricant, and very little, if at all, upon the nature of the surfaces in contact, it cannot be too clearly understood that, at low speeds and with heavy loads, this is by no means the case, and that so much injury may be done at starting that even if the surfaces do not seize, they may be made so uneven that the liquid film cannot be properly formed between them at high running speeds, and the friction, owing to the formation of a thin film of irregular thickness, may become so great that undue heating will result.

The effects at low speeds are practically the same whether the surfaces be plain, cylindrical, or of double curvature. In this respect again the laws of low speed friction differ from those obtaining at high speeds, for at high speeds the magnitude of the coefficient

depends upon the shape of the surfaces as well as upon the nature of the lubricant, etc.

The great frictional resistance met with at low speeds is well known to all who have noticed heavy machinery running slowly, or who have seen hydraulic pumping engines start from rest. In the latter case, from the moment the engine commences to move, it has to deal with the full load on all its bearings. In consequence of this all the faces are firmly pressed together, and the lubricating film, especially if it be a mineral oil, is not sufficiently thick to prevent even the minute irregularities of the surfaces from interlocking somewhat, and the bearings often 'groan' and the parts move by jerks. But as the speed increases this jerky motion decreases, the machinery 'groans' less and less, and finally moves easily and noiselessly. At the lower speed the lubrication is imperfect, but by the time the relative speeds of the rubbing surfaces have reached 10 or 20 feet per minute, comparatively thick films of oil have been thrust by the motion of the shafts, etc., between them and their bearings, and the load is carried by oil films only. When these comparatively thick films have formed, and the faces either wholly or over the greater part of their surfaces have separated, the lubrication is said to be 'perfect.'

Influence of the Viscosity and Oiliness of the Lubricant.—At low speeds, especially under heavy loads, and in all cases where a complete oil film cannot form between the friction surfaces, the viscosity and the oiliness (*lubricity, unctuosity*) of the lubricant are of great importance. These properties, though distinct, are related in some way, for it will generally be found, with oils of the same class, that the friction-reducing power at low speeds is in the same order as the viscosity, though in comparing mineral oils with animal and vegetable oils of the same viscosity the latter will be found to have the greater friction-reducing power, owing to their greater oiliness.[1] Some experimental results illustrating these facts are recorded in Tables XCI. c, and D (p. 345). Everything depends, however, upon the speed and the load; for, from the moment the surfaces commence to move relatively to each other, the oil tends to be forced between them and, therefore, as the speed increases and the film becomes thicker and more complete, so the reduction of friction becomes more and more dependent upon the viscosity and less upon the oiliness of the lubricant employed.

Influence of the Method of Lubrication.—The friction is much less dependent upon the method of lubrication at low speeds than at higher speeds; indeed, with a short chord of bearing surface, and therefore with heavy loads per square inch, the friction is approximately the same whether the pad, oil-bath, or other system of

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[1] Some authors use the term 'body' to signify the property of oiliness, but by others this term has been employed to mean viscosity, combined capillarity and viscosity, etc.

lubrication be adopted. With less heavy loads the friction is more variable.

The following results were obtained by Goodman [1] :—

TABLE V.—FRICTIONAL RESISTANCES AT A SPEED OF 7·8 FEET
PER MINUTE.

System of Lubrication.	Length of Chord of Bearing Surface (inches).				
	2·0	1·75	1·5	1·0	0·5
	Mean Frictional Resistances.				
Oil-bath, . . .	0·92	0·70	0·64	0·48	0·47
Saturated pad, . .	1·13	0·92	0·72	0·48	0·46
Oily pad, . . .	1·87	1·25	0·94	0·57	0·51

Coefficient of Friction at Low Speeds.—Experiments on the coefficient of friction at very low speeds have been made by Jenkin and Ewing,[2] who measured the friction at such low velocities as 0·0002 feet per second. They employed very considerable loads, and their bearing surfaces were spindles resting upon flat surfaces. These conditions were found by Kimball to favour a coefficient decreasing continuously with increase of speed.

Jenkin and Ewing state that in the case of steel upon brass, lubricated with oil, the coefficient was found to be 0·146 at all speeds from 0·0002 to 0·0064 feet per second. In the case of steel upon steel, however, the coefficient increased from 0·119 at 0·0002 feet per second to 0·13 at 0·0046 feet per second. This increase, and also a subsequent decrease of the coefficient of friction with increasing speed, is much more clearly brought out by Kimball, whose apparatus is thus described :—

"A shaft one inch in diameter was adjusted so that it could be driven at almost any rate between one revolution in two days and a thousand in a minute. A hole was bored through a block of cast iron $3\frac{1}{2}'' \times 3\frac{1}{2}'' \times 1\frac{1}{2}''$ and carefully fitted to the shaft; rigid iron rods were screwed into the top and bottom of this block, and adjusted so as to stand in a vertical line at right angles to the shaft. Upon these rods slotted weights could be placed, and thus the pressure upon the shaft and the centre of gravity of the brake could be readily adjusted."

[1] *Friction and Lubrication of Cylindrical Journals* (pamphlet), 1890, p. 133.
[2] *Phil. Trans.*, 1877, p. 509.

The two following tables give the results obtained :

TABLE VI.

Feet per Minute.	Cm. per Second.	Relative Values of Friction Coefficient.
·00058	·000295	0·37
·00225	·001144	0·51
·00500	·002540	0·73
·01100	·005590	1·00

These results show a coefficient *increasing* as the velocity increases.

TABLE VII.

Feet per Minute.	Cm. per Second.	Relative Values of Friction Coefficient.
6·0	3·05	1·00
22·6	11·49	0·60
50·4	25·61	0·46
110·0	5·90	0·29

These results show a coefficient *decreasing* as the velocity increases.

That the coefficient of friction of lubricated bearings at very low speeds is often greater than the static coefficient is supported by many other facts. Goodman's experiments (Table VIII. p. 61) may be instanced. On the diagram, fig. 23, the curve A shows the manner in which, in these experiments, the friction varied at moderately low speeds with a load of 150 lbs. per square inch. If the curve A were continued so as to cut the ordinate of no speed, the static coefficient would be about 0·21. This is for bath lubrication. With saturated pad lubrication (curve B) the static coefficient would be about 0·27. These are high figures when compared with the static coefficients obtained by Thurston, which are given on the diagram, fig. 22. It is probable that had Goodman experimented at much lower speeds, he would have found that the friction assumed a maximum at a comparatively low velocity, and then decreased again as the speed decreased. Wellington's results [1] were obtained by noting the resistance offered to the motion of wagons, and cannot be considered as accurate measures of journal friction at very low speeds, as the resistance was due partly to the *rolling* friction of the wheels on the rails, partly to vibration, etc. With lubricated journals it would appear that the coefficient of friction is at a maximum at some speed below one centimetre per second (= about 2 feet per minute). Kimball [2] says that an increase in the pressure between the surfaces

[1] *Trans. Amer. Soc. Civ. Eng.*, 1884.   [2] *Amer. Journ. Science*, 1876.

Coefficients of Friction.
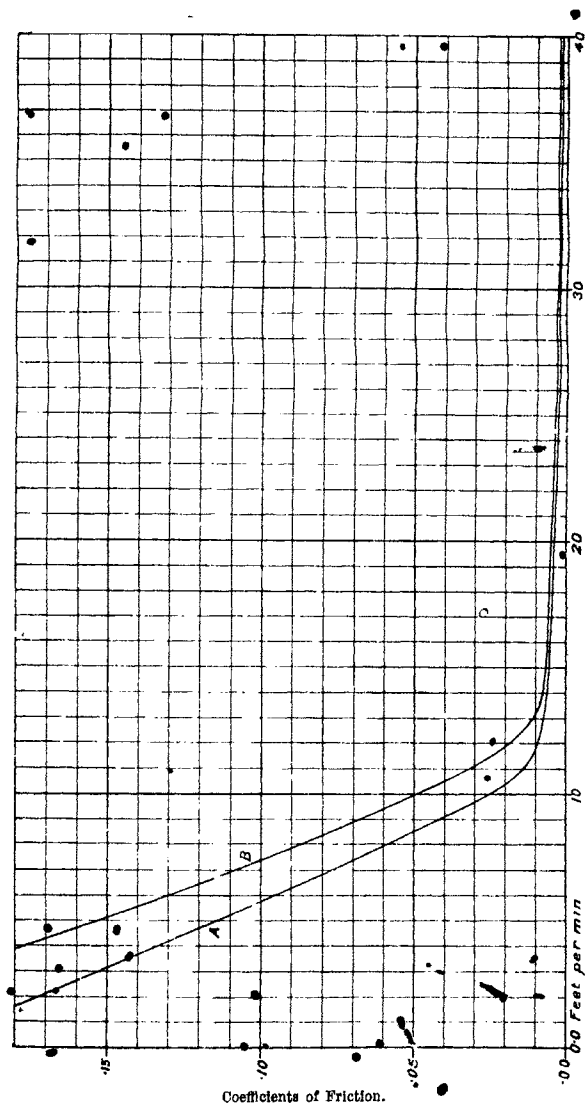
in contact changes the value of the maximum coefficient, and makes it correspond to a smaller velocity. The more yielding the materials between which the friction occurs, the higher is the velocity at which the maximum coefficient is found. Heating the bearings changes the position of the maximum coefficient to a higher velocity. In the vicinity of the maximum coefficient, the friction generally remains sensibly constant for a considerable range of velocities. With speeds above one centimetre per second, or thereabouts, a viscous lubricant being used, the friction of journals falls rapidly until a velocity of about five centimetres per second (= about 10 feet per minute) is reached, and then increases very slowly to the highest speeds at a rate depending upon the method of lubrication employed. This change of the coefficient of friction with increasing speed is shown on the diagram, fig. 24. From a to b the curve rises, indicating that at the lowest speeds, below one centimetre per second, the coefficient
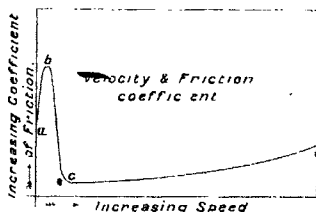
Fig. 24.

of friction increases with increasing speed. With further increase of speed, the coefficient of friction rapidly decreases and reaches a minimum (at c), if the lubrication is good, at a speed of about five centimetres per second; it then slowly increases again. With imperfect lubrication, or with plastic lubricants, the coefficient of friction falls less rapidly from b; indeed, the speed may reach 100 feet per minute before the lowest point c of the curve is reached.

At one time it was supposed that there was always a sudden change in the value of the coefficient of friction when the surfaces in contact came relatively to rest. This was shown to be erroneous by Jenkin and Ewing, who found that although the frictions of rest and of motion have often very different values, in no instance was there a sudden or abrupt change in value, the kinetic coefficient gradually changing as the speed decreased until the static coefficient was reached. Their experiments were made at extremely low velocities, as stated on p. 57, and from the results obtained we may safely conclude that the coefficient gradually changes when the velocity becomes small, so as to pass without discontinuity into the friction of rest.

Subsequent experiment has amply confirmed this view. Still our knowledge of the variations which the kinetic friction undergoes with change of speed is by no means complete, few experiments having been carried out at very low velocities.

In Table IX. (p. 70) which will be fully described later, the value of a certain constant, C, leads to the belief that, as in the case of cylindrical surfaces the lubrication of plane surfaces is also imperfect at low speeds and with heavy loads. When the value of C ceases to

vary, the pressure film has, there is every reason to believe, established itself.

At a mean speed of about 60 feet per minute, and with greater loads than 60 lbs. per square inch, the pressure film is partly *crushed* out and the friction becomes abnormally great, as shown by the large and increasing value of C. At 90 feet per minute, even 160 lbs. per square inch is satisfactorily carried, but at speeds below 13 feet per minute, even with 20 lbs. per square inch, the pressure film is not properly formed and the friction is high.

TABLE VIII.[1]—CHANGES IN VALUE OF THE COEFFICIENT OF FRICTION WITH INCREASING SPEED.

SPEED	Coefficients of Friction (μ_1) under a pressure of		
Feet per Minute.	50 lbs. per sq. in.	75 lbs. per sq. in.	150 lbs. per sq. in.
5	...	·0025	·1145
10	·0009	·0007	·0250
15	·0012	·0008	·0351
20	·0014	·0009	·0034
25	·0017	·0011	·0027
30	·0021	·0013	·0023
40	·0026	·0016	·0019
50	·0032	·0018	·0017
70	·0042	·0024	·0017
90	·0053	·0030	·0020
110	·0064	·0036	·0024
130	·0075	·0042	·0029
150	·0086	·0048	·0035
170	·0096	·0054	·0041
190	·0106	·0060	·0047

In the case of a journal, the high coefficient of friction at low speeds is also very striking, especially when the load per square inch is considerable. Table VIII. shows the changes in the value of μ_1 with increasing speed when the pressure is 150 lbs., 75 lbs., and 50 lbs. per square inch, and the journal flooded with the lubricant. With the smaller load, even at such a speed as 10 feet per minute, the coefficient of friction is small. At 75 lbs. per square inch the friction is at a minimum between 5 and 10 feet per minute, whilst at 150 lbs. per square inch the minimum frictional resistance is not reached until a speed of about 40 feet per minute is attained. In other words, the lubrication, except with small loads, is imperfect at low speeds, a high speed being required to form a sustaining liquid pressure-film.

Although the above statements concerning the changes which the low speed friction undergoes with slight changes of speed are doubtless

[1] These figures have been obtained by plotting the values given in Goodman's tables.

corrèct for certain conditions, the effects produced by changes in the viscosity and other properties of the lubricant, the method of its application, and the form and condition of the rubbing surfaces, are only imperfectly known. Neither has the action of a lubricant in decreasing friction, when the speeds of rubbing are small, been subjected, nor does it appear to be amenable, to mathematical treatment. However, the conditions obtaining under such circumstances can be given approximately.

Theory of Low Speed Lubrication.—We have already pointed out that if the irregularities of the surfaces did not interlock, the friction would be much smaller than it really is at very low speeds; indeed the friction at rest, if the viscous lubricating film were sufficiently thick to prevent interlocking, would be nil. We may, therefore, assume that the surface irregularities are large as compared with the thickness of such a lubricating film, and that as the speed increases the film becomes thicker.

The action will be understood from fig. 25, which shows a highly magnified section of two imaginary surfaces in slow relative motion, prevented from touching by a viscous lubricating film. As the

Fig. 25.

surfaces move over each other the elevated portions alternately approach and recede, and the greater the relative speed the more rapid is this action. Each time two such elevated points as A and B approach, the liquid is expelled from between them, and then drawn in again as they recede from each other. But the viscosity and oiliness of the lubricant resist this alternate squeezing out and drawing in of the film more and more powerfully as the speed of rubbing increases.

The more rapid the relative movement, the smaller is the volume of lubricant forced from between the asperities, and the thicker the film becomes. Even at very low speeds this thickening of the film is assisted by the lubricant which is *trapped* at the front edge of the bearing. This point will be dealt with at a later stage, as to it must mainly be ascribed the low friction of even flat surfaces at high speeds. The thickening action occasioned by the asperities passing over each other can only occur to a very limited extent, and would seem to prevent the kinetic friction at *very low* speeds from exceeding the static friction by so much as it otherwise would.

The resistance due to the viscosity of the film is proportional to the speed of rubbing, and inversely proportional to the thickness of the film. Up to speeds somewhat below one centimetre per second we must, therefore, assume that the lubricating film does not thicken with sufficient rapidity to prevent the speed from increasing the frictional resistance. At greater speeds, however, the film thickens so rapidly, as compared with the increase in speed, that the coefficient soon falls to a small fraction of its original value.

Within certain limits, the smoother the surfaces the smaller the static coefficient; but at very low speeds such surfaces give comparatively high frictional resistances, for the films are then exceedingly thin, and are not increased in thickness much by the action above described.

Lubrication with Plastic Solids.—For a number of years greases were almost exclusively used for railway axles. They are generally emulsions of fat or oil, soap and water. Such axle greases are plastic rather than viscous mixtures, and require the exertion of a certain definite pressure to cause them to flow. Owing to this fact, they cannot be completely squeezed out from between the journal and its bearing They are, on the other hand, readily forced in at the higher velocities. Although offering much more resistance to motion at high speeds than does a lubricant of low viscosity, the much greater thickness of the plastic film, when the speed is low, makes the static friction less than is given by most, if not by all, truly viscous fluids. On this account, although the friction of a rapidly moving train lubricated by oil may be much less than when plastic greases are used, a much greater force is required to set the coaches in motion. Greases have consequently maintained their position as lubricants for low speed goods trains on most lines.

T. G. Clayton[1] made a series of experiments to ascertain the friction of coaches belonging to various railway companies with a view to measuring the static friction when using oil and grease, respectively, as lubricants. He found that, on the average, a tractive force of 12·62 lbs. per ton was required to move a coach when lubricated with grease, whilst a force of 18·54 lbs. per ton was required when oil was used.

To keep the rubbing surfaces of bearings from coming into contact, owing to the expulsion of the lubricant by the load when their relative velocities are small, oils, fats and greases containing solid lubricants, such as graphite, are much more extensively used than are such solids alone. As a rule, the viscous or plastic matrix acts as a carrier for the solid lubricant, and enables it to be more readily applied to the rubbing surface. It is placed in such a position, with regard to the bearing, that should the liquid lubricant be rubbed out, the heat arising from the increased friction melts the matrix, and the mixture, containing the solid in suspension, immediately runs on to the dry surface.

Such mixtures are mostly suitable for heavy pressures and low speeds. At high speeds their frictional coefficient is very great, and the heating and loss of power which they cause is proportionately serious. Their use is, therefore, almost entirely restricted to bearings which are only in motion occasionally, or to such as the journals of tip wagons, or the axles and spindles of hauling machinery.[2] The

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[1] *Lubrication and Traction relating to Railway Carriages* (pamphlet). William Clowes & Sons, 1892.

[2] Further information on the use of grease for locomotive axles is given on p. 467.

solid portion of the lubricant finds its way into the surface irregu-
larities and fills them up, thus increasing their smoothness. It also
prevents the metals from welding to each other at points where they
are forced into contact by excessive pressure. Solid lubricants are
often mixed with liquid ones and used for rubbing surfaces which
have not properly worn themselves true, for although the coefficient
of friction may be high, and the bearings become heated, the solid
lubricant prevents the injury that would otherwise result from the
decreased viscosity of the liquid. Thus graphite, soapstone, and
paraffin wax melted together and worked, while hot, into a plaited
rope of cotton, jute or hemp, constitute an excellent packing for
piston-rod and other glands. The wax keeps the packing soft and
pliable, the soapstone and graphite serve to make it durable, whilst
the fibrous material binds the whole together and gives it a form
convenient for the user.

High Speed Lubrication.—*The Pressure Film.*—At a speed depend-
ing greatly upon the load and the nature of the lubricant, the rubbing
surfaces commence to separate, and a comparatively thick *pressure
film* forms between them and carries the load. The extent to which
the thickness of this film increases with the speed varies not only
according to the load, the viscosity of the lubricant, the area of the
bearing, and the speed, but also according to the shape of the
surfaces and the relative positions they assume. As illustrations of
the conditions under which pressure films are produced, and those which
determine their thickness, it will be convenient first to consider the
case of parallel plane surfaces, then of plane surfaces inclined to each
other, and finally of cylindrical surfaces such as those of journals.

Lubrication of Parallel Plane Surfaces.[1]—Although neither a very
common form of bearing nor one that will carry very great loads, the
conditions which obtain when parallel plane surfaces are pressed
together, and caused to slide over each other, are of considerable
interest, for the laws which govern the frictional resistance in such
cases serve to illustrate very clearly the mode in which viscous
substances reduce the friction between relatively moving bodies.

The subject was one that engaged the close attention of
Beauchamp Tower. Indeed, had it not been for his experimental
work, to which reference has already been made, we should have been
without the data upon which to found a hydro-dynamical theory.
Of the experiments made by Tower, those on pivot friction have most
bearing upon the subject in hand.

In these experiments, faces which were free to move to or from
each other were maintained parallel. The pivot experimented with
was made of steel, had a perfectly flat end 3 inches in diameter, and
was pressed against a manganese bronze bearing in such a manner
that the faces, although they could separate, were always parallel to
one another. The exact form of bearing and the details of the
machine employed are given on pp. 367–8. The lubricant was supplied

[1] Deeley and Wolff, *The Engineer*, 10th January 1896, p. 25.

through a hole in the centre of the bearing, and was distributed by
two radial grooves extending from the centre hole to within a $\frac{1}{16}$ of
an inch of the periphery of the bearing surface. In this way the
bearing was always kept flooded with oil, which remained clean and
bright during the experiments, indicating that no abrasive action
was taking place. In other words, the lubrication was 'perfect'; *i.e.*
there was a comparatively thick film of oil maintained under pressure
between the surfaces, which were thus prevented from touching each
other. To the viscous action of this oil film the friction was wholly
due, being smaller the thicker the film, and greater the higher the
speed. However, with each change of speed or load a corresponding
change in the thickness of the film, and therefore of the frictional
resistance, took place.

Fig. 26 illustrates the action of such a film. It shows two
parallel planes of unlimited length and breadth separated by a viscous
film of thickness r_0. The upper plane CD is supposed to be *fixed*,
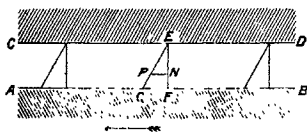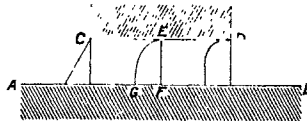
FIG. 26.   FIG. 27.

while the lower plane AB moves in the direction of the arrow with a
velocity v_1. By the definition of viscosity (p. 18) there will be a
tangential resistance to motion

$$f = \eta \frac{v_1}{r_0} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

η being the viscosity of the liquid. When one plane has an area A,
the total resistance to motion

$$F = \eta \frac{v_1 A}{r_0} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

The tangential motion varies uniformly from v_1 at AB to nil at
CD. Thus, if the length FG be taken to represent v_1, then the
length of the line PN will represent the velocity at P.

When first the planes are set in motion, the inertia of the viscous
liquid prevents it from at once assuming this condition of flow but in
a comparatively short period all irregularities of motion subside, and
the velocity of the liquid at any plane is strictly proportional to its
distance from CD.

Inertia effects also show themselves when one plane is of finite
extent. They tend to throw the surfaces apart, and maintain a film
of the liquid between them. In fig. 27 the surface CD is supposed to
be of limited length, both parallel with and in a direction perpen-

dicular to the paper. AB is flooded with oil, which when approaching, but at some distance from D, is moving at the speed v_1 of the plane AB. Just before reaching D, a relative motion or distortion of the fluid is produced. At D the oil in actual contact with the fixed plane is at rest, and the remainder, instead of passing along between the surfaces in such a manner that the *rate* of distortion is everywhere the same, as in fig. 26, is caused by its own inertia to enter the space between the planes, and to flow in such a way that—as shown in fig. 27—the rate of distortion becomes much greater near the plane CD than near the plane AB; whilst, at the end C, the rate of distortion of the lubricant, in virtue of its viscosity, may have become approximately the same at all planes. Under these conditions, therefore, the lines EG are curved, the rate of distortion is greater near CD than near AB, and the volumes passed at each section are proportional to the areas enclosed by EFG. It will be noticed that these areas are larger at the entrance D than at the exit C, part of the excess of liquid escaping laterally, owing to the comparatively small width of the plane CD in a direction perpendicular to the surface of the paper. When the velocity with which the lower plane moves is very small, the volume carried in between the surfaces is nearly proportional to $\dfrac{EF \cdot GF}{2}$ and at the opposite end of the plane the same volume is carried out; but as the speed increases, the volume introduced may exceed the volume carried out at C by an amount almost proportional to $EF \cdot GF - \dfrac{EF \cdot GF}{2}$

$$= \frac{EF \cdot GF}{2},$$

at which the excess remains unaltered, however much the speed may be increased.

When the planes are of considerable area, and are close together, the viscosity of the oil powerfully resists its escape at all points, and at the same time, by tending to make the rates of distortion everywhere equal, causes it to accumulate and force the planes apart until the forces are in equilibrium. This action is going on at all points between the surfaces when their length, measured in the direction of motion, is not very great. The force tending to throw the planes apart is, therefore, distributed over them much as is the force resisting the approach of two surfaces separated by a viscous medium.

In this way, when the opposing surfaces are kept parallel, a pressure film is maintained between them, and a considerable load may be supported by CD, so long as AB is in rapid motion. The resistance to the motion of the lower plane is then due wholly to the viscosity of the liquid film. It is, however, somewhat in excess of the value obtained by the formula $F = \eta \dfrac{v_1 A}{r_0}$, for owing to the excess of oil introduced at D, the conditions of motion are not exactly

those shown in fig. 26. •No correction for this small difference will be attempted.

We will in the first place deal with the conditions determining the volume V, introduced through the relative motion of the surfaces and the density of the liquid. The viscous liquid resting upon AB at points distant from the surface CD, is moving with a velocity r_1. At the point D, when the velocity is considerable, the liquid is *thrown* against the opening between the surfaces, much in the same way as water from the combining cone of an injector is thrown against the orifice of the delivery cone. Its power of entering the opening may be regarded as proportional to the density of the liquid and to the square of the velocity. It is almost independent of the viscosity; for the entrance of the liquid is as much opposed by its adherence to CD as it is assisted by its adherence to AB.

No doubt, at low speeds, as the load urging the faces together is increased, the volume entering decreases more rapidly than does the distance separating the rubbing surfaces, until finally the marginal pressure of the imprisoned film prevents the liquid from entering at all, and the faces close together; but when the speed is great and the load is increased, there is reason to suppose that the liquid fails quite suddenly to get between the surfaces, which thereupon 'seize.' We may therefore assume that, except at low speeds, the volume, V, entering is approximately proportional to $v_1 r_0 b$, where r_0 is the distance between the surfaces and b the length of the orifice at D.

In the case of a rectangular bearing, the viscous liquid is introduced along one side and escapes along the margin of the other three, and the larger the volume introduced, the more the bearing surfaces part in order to allow it to escape.

The conditions attending the escape of the fluid may, therefore, be well illustrated by taking the case of parallel surfaces approaching each other without tangential motion (fig. 28).[1] The fluid has to be *squeezed out* from between the surfaces, and since there is no motion of the fluid in contact with the surfaces, the horizontal velocity will be greatest half-way between them, nothing at O (the middle of CD), and greatest at the ends. This is for planes of infinite length in a direction

FIG. 28.

perpendicular to the plane of the paper. If in a certain state of motion—shown by the dotted lines in fig. 28—the space between AB and CD be divided into ten equal parts by vertical lines, and if those lines be supposed to move with the fluid, they will shortly after assume the positions on the curved lines, in which the areas included between each pair of curved lines is the same as in the
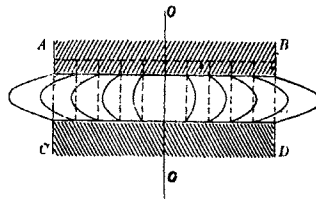
[1] Osborne Reynolds, *Phil. Trans.*, 1886, p. 173.

dotted figure. If it were not for the inertia of the fluid, the lines would be absolute, instead of approximate, parabolas. It can be at once seen that the curved lines indicate the rates of distortion at different points, and, as force is required to maintain the rate of distortion at each plane constant, a vertical pressure, W, must be applied to force the liquid out. The pressure will be greatest at O, and will fall off towards the ends C and D.

In the case of an ellipse of semi-axes a and b, it follows from Osborne Reynolds' equations that the velocity of normal approach is proportional to $\dfrac{r_0{}^3 W(a^2 + b^2)}{a^3 b^3 \eta}$.

Therefore, the escaping volume may be written

$$V_1 = k \frac{r_0{}^3 W(a^2 + b^2)}{a^2 b^2 \eta} \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

We thus obtain expressions for the volume, V, of the viscous liquid introduced by the motion of the bearing, and also for the motion, V_1, of the liquid pressed out by the weight on the brass. In order that the conditions of flow may remain constant, these two values must be equal, consequently,

$$V = V_1 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

$$= v_1 r_0 h = k \frac{r_0{}^3 W(a^2 + b^2)}{a^2 b^2 \eta} \qquad . \qquad . \qquad . \qquad (6)$$

and

$$v_1 = k_1 \frac{r_0{}^2 W(a^2 + b^2)}{a^2 b^3 \eta} \qquad . \qquad . \qquad . \qquad (7)$$

Therefore,

$$\frac{v_1{}^2 \eta^2 a^2 b^2}{r_0{}^2} = k_1 \frac{v_1 W(a^2 + b^2)\eta}{b} \qquad . \qquad . \qquad . \qquad (8)$$

The left-hand term of this equation gives us the value of F^2 required to maintain the plates in steady motion, since F (equation 1) is inversely proportional to r_0 and directly proportional to $v_1 \eta a$.

$$\therefore F \propto \sqrt{\frac{v_1 W(a^2 + b^2)\eta}{b}} \qquad . \qquad . \qquad . \qquad (9)$$

which, in the case of a circle, when $b = a$, resolves itself into

$$F \propto \sqrt{v_1 W b \eta} \qquad . \qquad . \qquad . \qquad . \qquad (10)$$

and, as the coefficient of friction (μ_1) is equal to the resistance F divided by the total load,

$$\mu_1 = \frac{F}{W} = c \sqrt{\frac{v_1 \eta b}{W}} \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

The values of F and the coefficient of friction will, therefore, vary with the shape of the surface boundary, but will be constant for surfaces of similar shapes. Hence, in the case of the circle, ellipse, and rectangle, we see that, the proportions being unaltered, and the premises correct, the friction varies as the fourth root of the area of the surfaces.

Experiment appears to bear out this statement, for it has been

found that the coefficient of friction of a pivot or plane surface is affected much less by the size of the bearing than by the velocity at which it runs or by the load which it carries, the pressure film being unbroken.

Although in Tower's experiments every care was taken to measure the friction between the surfaces, and to keep them in good condition, no attempt was made to ascertain the rise of temperature produced by different speeds and loads, or the value of the viscosity of the oil used. Some resistance to motion must also have been offered by the oil film surrounding the cylindrical portion of the footstep, but as the clearance is not given, and we do not know the viscosity of the oil, its magnitude cannot be calculated.

We are consequently unable to compare one experimental result quite satisfactorily with another.

Assuming that the oil did not vary very much during the trials, and that the cylindrical footstep was a moderately loose fit in the brass, we may write from (11)

$$C = F \sqrt{\frac{1}{NW}} \qquad . \qquad . \qquad . \qquad . \qquad (12)$$

N being the number of revolutions of the footstep, and C a constant.

In Table IX. are given the values of C, calculated from Tower's experimental results, the mean speeds of the footstep, the loads, and the frictional resistances. At low speeds, C has a high value, which increases steadily as the load increases, showing that the volume of oil entering is not proportional to $EF . GF$, and is not keeping the surfaces properly apart. At higher speeds, however, C actually decreases somewhat, until the heaviest loads are reached. The decrease is probably brought about by the heating effect of the friction decreasing the viscosity of the lubricant, o· by the fact that the force measured in the experiments was partly due to the viscous resistance of the oil film surrounding the cylindrical portion of the footstep. In all cases, the highest loads cause a small increase in the value of C, in spite of the fact that the viscosity of the lubricant must have been lowered by the heat generated by friction. Under these conditions the film would be thin, and the volume of liquid introduced by its inertia somewhat less than when r_0 is large.

Lubrication of Inclined Plane Surfaces.—As a rule, even when the rubbing surfaces are plane, the opposing surfaces are free to adjust themselves according to the position of the load they carry and the distribution of pressure in the film keeping them apart. The conditions under which the lubricant then acts differ somewhat from the case of parallel plane surfaces. In the latter case, it is to the *inertia* and *viscosity* of the lubricant that we must attribute the presence of the pressure film; but when the faces are able to become inclined, the liquid wedges itself between them and forces them apart. The conditions then obtaining have been carefully considered by Osborne Reynolds, and merit close attention, as it is

TABLE IX.—VALUES OF 'C' FROM BEAUCHAMP TOWER'S EXPERIMENTS.

Load.	50 Revs. per Min. 1309 Feet per Min.		128 Revs. per Min. 33·51 Feet per Min.		194 Revs. per Min. 58·23 Feet per Min.		290 Revs. per Min. 75·08 Feet per Min.		353 Revs. per Min. 92·41 Feet per Min.	
Lbs. per sq. in.	Inch-lbs.	C.	Inch-lbs.	C.	Inch-lbs.	C.	Inch-lbs.	C.	Inch-lbs.	C.
20	2·77	·087	1·13	·0223	1·44	·0231	2·51	·0294	2·36	·0281
40	4·61	·103	1·54	·0215	1·74	·0197	3·03	·0282	2·72	·0229
60	7·07	·129	2·26	·0258	2·15	·0199	3·33	·0252	3·08	·0212
80	10·25	·162	3·59	·0355	2·56	·0206	3·64	·0239	3·59	·0214
100	15·48	·218	5·48	·0484	3·13	·0225	3·95	·0232	4·00	·0213
120	18·72	·241	7·02	·0566	4·41	·0289	4·10	·0219	4·51	·0219
140	...	...	9·23	·0690	6·10	·0370	4·51	·0224	5·23	·0235
160	...	...	12·82	·0897	7·69	·0427	5·03	·0233	6·15	·0252

to this action that he ascribes the great carrying power of cylindrica bearings.

As to the frictional resistance and carrying power of plan surfaces, such as engine slide blocks, which become slightly incline to each of the faces they run upon, no experimental results have ye been obtained which can be compared as regards accuracy wit Beauchamp Tower's tests of pivot bearings.

In fig. 29, AB is a plane surface, of unlimited length and breadth, moving in the direction of the arrow beneath the inclined surface CD, which is of limited length and of very limited breadth, in a direction perpendicular to the paper. Omitting the effects which would be produced by the inertia of the liquid, the conditions of flow are as follow :—
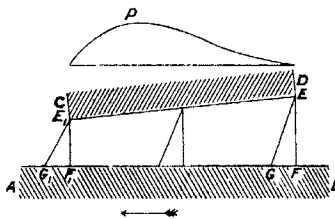
Fig. 29.

At the lower edge of D, where the liquid enters between th surfaces, the volume introduced is proportional to $\frac{EF \cdot GF}{2}$.

However, owing to the inclination of the surfaces, the volum passed out at the edge C is only proportional to $\frac{E_1F_1 \cdot G_1F_1}{2}$.

When the surface CD is of considerable area, and the planes are ver close together, the excess of oil or other lubricating fluid introduce at the edge D must escape ; but this is opposed at all points by th viscosity of the liquid. The oil, therefore, tends to accumulate, an a pressure is set up which forces the surfaces apart until the load sufficient to prevent further recession. In this respect, the action similar to that we have already described as resulting from the inerti of the entering fluid.

According to Osborne Reynolds, the effect reaches a maximum fo bearings of such dimensions as are used in practice when $EF = 2$ E_1F_1, and owing to the greater freedom with which the lubricar can escape at the end D and the sides near it, the point of maximum pressure p is somewhat nearer C than D. The curv at the top of the figure indicates, approximately, the pressure a different points of such a film, tending to force the surfaces apar The direction in which the load acts, normal to AB, does no necessarily coincide with p, but with the centre of the area enclose by the curve and base line of the pressure ordinates.

The pressure exerted by the film must always be equal to th resultant external force which, neglecting the obliquity of CD, perpendicular to AB, and tends to force the surfaces together. Whe the surfaces are free to assume any position, the pressure of the fil inclination of surfaces, etc., adjust themselves to suit the load a

its point of application, and the nearer the surfaces are caused to approach each other, the greater is the friction and consequent pressure for the same velocity.

The relations obtaining between the load, pressure, etc., under these circumstances, have been determined by Osborne Reynolds.

In the case of a surface CD of infinite width in a direction perpendicular to the paper he makes

$$r_1 = k_1 \frac{r_0^2 W}{\eta a^3} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (13)$$

and the force required to keep them in relative motion [1]

$$F = k_1 \frac{\eta a v_1}{r_0} \qquad . \qquad . \qquad . \qquad . \qquad (14)$$

Therefore,

$$\frac{v_1^2 \eta^2 a^2}{r_0^2} \propto \frac{\eta v_1 W}{a} \qquad . \qquad . \qquad . \qquad . \qquad (15)$$

and

$$F \propto \sqrt{\frac{\eta v_1 W}{a}} \qquad . \qquad . \qquad . \qquad . \qquad (16)$$

Lubrication of Cylindrical Surfaces.—The cylindrical is by far the most common form of bearing surface, and is the one with which most of the experiments recorded have been made. Until Beauchamp Tower's results were published, little was really known concerning the effects produced by varying the method of applying the lubricant. He showed that many of the methods in use were very imperfect, the oil holes and oil ways often cutting across those portions of the surfaces where the pressure of the film should be at its greatest, and allowing the lubricant to escape. With properly-shaped brasses resting upon well lubricated journals, he succeeded in obtaining results which were proved by Osborne Reynolds to be in accordance with hydro-dynamical theory. The method of applying the lubricant, and the machine with which he experimented, are described in Chapter IX.

A brass which has been running for some time upon a lubricated cylindrical journal wears in such a way that the radius is always slightly greater than that of the journal. When forced into contact, therefore, the brass and journal do not touch over the whole of their surfaces. On the other hand, when the journal is in rapid motion,

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[1] It must be clearly borne in mind that the load carried may be modified very largely by varying the direction in which it acts, for the inclination of the surface varies according to the distribution of the pressure, etc. Both in the case of inclined and parallel surfaces inertia effects, previously considered, must show themselves. The wedging and the inertia actions, however, as will be seen from equations (15) and (16). have similar effects upon the relationships between the coefficient of friction, the speed, the load, and the viscosity; but the relationships between these values and the area and shape of the bearing do not appear to be *quite* similar. Still it is clear that, as is the case with contaminated and clean surfaces, the coefficient of friction of parallel plane surfaces is only slightly affected by variations in the area of the surfaces in contact.

if the weight on the brass is not too great, the surfaces are separated from each other by a continuous oil film. Fig. 30 represents, in an exaggerated manner, a section through such a brass and journal, the latter being supposed to rotate in the direction shown by the arrow

The curved surfaces AB and CD have their centres at I and J, a line drawn through which indicates the position of nearest approach F_1F_1. Between EF and E_1F_1 the distance separating the surfaces decreases, the triangle $E_1F_1G_1$ is consequently smaller than EFG, and therefore the lubricant which is brought up by the rotation of the journal and forced into the narrow space between the journal and the brass becomes compressed in its passage forward and tends to force the surfaces apart. On the other hand, as we go from $E_1F_1G_1$
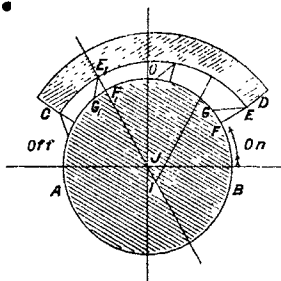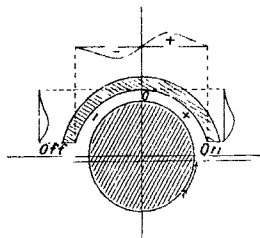
FIG. 30.   FIG. 31.

towards C the faces recede, and were it not for the flow of oil from the portion where the liquid undergoes compression, the pressure might be, and, indeed, sometimes does become, negative.[1]

When there is no load, the conditions are as illustrated in fig. 31. Here the vertical pressures are shown by the curved lines on the top of the figure. On the right-hand or 'on' side the pressure is positive, whilst on the left-hand or 'off' side it is negative, and the vertical components of these pressures balance each other. On the other hand, the horizontal component of the pressures to the left and right, indicated by the curves at the sides, will both act on the brass to the right, and as these will increase as the surfaces approach, the distance corresponding to JI (fig. 30) must be exactly such that these components balance the resultant friction.

The thickness of the film at different points, and the variations of

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[1] In the *American Machinist* for Sept. 10 1903, H. F. Moore states that in conjunction with G. A. Morgan he constructed a small dynamo, in which the bearings entirely surrounded the journal. By simply leading a pipe from a reservoir of oil to that part of the bearing where the pressure would be negative, if anywhere, it was found that the bearing would suck in oil from a reservoir six inches below, and thus lubricate itself.

the position of E_1F_1 with different loads, have been worked out mathematically by Osborne Reynolds, whose exact equations give results which agree very closely with the experimentally ascertained facts. For the full treatment of the subject the original papers should be consulted, as the results only can be given here.

Influence of Load and Speed.—In the case of *plane surfaces, whether parallel or inclined, the frictional resistance is proportional to the square root of the load.* Cylindrical surfaces, however, owing to their curvature, cannot separate sufficiently, whilst still sustaining a load, to give this result, for when the load is increased E_1F_1 decreases, the lubricant is prevented from escaping on all sides as freely as before, and EF, *i.e.* the distance between the brass and journal on the 'on' side, increases. Consequently, as the load is increased, the positive vertical component to the right (fig. 31) increases and overbalances the negative component to the left, which decreases, and E_1F_1, the point of nearest approach, moves to the left until the load reaches a particular value; above this load the point of nearest approach moves back towards O. During this change in the position of E_1F_1, the thickness of the film at different points alters in such a way that the viscous resistance which it offers to the motion of the journal remains nearly constant: and *the friction of journals is, therefore, practically independent of the load when the speed is sufficient to maintain a pressure film between the two surfaces.*

According to this reasoning, the friction at high speeds and with perfect lubrication appears to be, *ceteris paribus,* approximately proportional to the area of the contact surfaces, the speed of the journal, and the viscosity of the lubricant, and nearly independent of the load.

Before the journal commences to rotate, the lubricant being a viscous one, the load will have brought the brass into contact with the former at O (fig. 31); but at the ends it will be separated by an appreciable space from the journal. *At starting, and at very low speeds,* the surfaces being in contact, there is friction of solid upon solid, *the coefficient of friction is large,* and the surfaces undergo some abrasion; but as the velocity of the journal increases, the surfaces gradually become separated by an oil film, more particularly if there be a plentiful supply of lubricant. Thickening of the film, as we have seen, can only take place to a limited extent, owing to the curvature of the surfaces, so that *with increasing speed the resistance becomes more nearly proportional to the speed and less affected by the load.* At the outset, as with plane surfaces, when the oil film has scarcely established itself, the friction, ceteris paribus, *varies with changes of load.* However, owing to the curvature of the surfaces, the film very quickly reaches a maximum thickness.

Table X. gives the results obtained by Beauchamp Tower with bath lubrication.

TABLE X.—BATH OF OLIVE OIL. TEMPERATURE 90° F.

Journal, 4 in. wide × 6 in. long. Chord of Arc of contact = 3·92 in.

Nominal Load. Lbs. per sq. in.[1]	Nominal Frictional Resistance per Square Inch of Bearing Surface.							
	105 ft. per Min.	157 ft. per Min.	209 ft. per Min.	262 ft. per Min	314 ft. per Min.	366 ft per Min.	419 ft. per Min.	471 ft. per Min.
520	...	·416	·520	·624	·675	·728	·779	·883
468	...	·514	·607	·654	·701	794	·841	·935
415	...	·498	·580	·622	·705	·787	·870	·995
363	...	·472	·580	·616	·689	·725	·798	·907
310	...	·464	·526	·588	·650	·680	·742	·835
258	·361	·438	·515	·592	·644	·669	·747	·798
205	·368	·430	·512	·572	·613	·675	·736	·818
153	·351	·458	·535	·611	·672	·718	·764	·871
100	·360	·450	·550	·630	·690	·770	·820	·890

[1] The nominal load per square inch is the total load divided by (4 × 6).

The loads ranged from 100 lbs. to 520 lbs. per square inch, nominal, and yet for each speed the frictional resistance was nearly constant. *Above speeds of 100 feet per minute low speed effects do not show themselves, and the coefficient of friction will be seen to be nearly proportional to the square root of the speed* instead of to the actual speed. Osborne Reynolds considers this as due to the fact that when the speed is increased the rate of shear which the film undergoes is likewise increased; the film becomes heated, its viscosity is decreased, and less resistance to motion is encountered.

Goodman has also published some results which he obtained with different speeds and different methods of lubrication, and which are given in the following table :—

TABLE XI.—RESISTANCE AT DIFFERENT SPEEDS.

Load, 300 lbs. Temperature, 40° C. Brass, ·5 in. × 4 in.

Oil Bath.		Saturated Pad.		Oily Pad.	
Feet per Min.	Coefficient of Friction, μ_1.	Feet per Min.	Coefficient of Friction, μ_1.	Feet per Min.	Coefficient of Friction, μ_1.
2·6	·1610	4·70	·1610	5·2	·1540
7·8	·0630	7·80	·0910	7·8	·0560
11·0	·0140	13·61	·0700	11·0	·0021
15·7	·0052	38·20	·0021	17·3	·0021
57·1	·0017	88·50	·0024	27·2	·0028
67·0	·0017	111·50	·0028	61·3	·0042
103·7	·0021	122·00	·0035	88·5	·0070
122·0	·0028	149·70	·0063	122·0	·0091
146·6	·0035	183·20	·0098	161·0	·0126
164·9	·0038	213·60	·0126	183·0	·0168
183·2	·0042	...	...	209·4	·0217
...	...	...	...	242·9	·0252

At the speeds printed in heavy type in this table the friction is high, owing to the pressure film not having been properly formed. At higher speeds, however, as found by Osborne Reynolds, the frictional coefficient is approximately proportional to the square root of the speed.

Comparison of Friction Coefficients of Journals, from the tests of "Thurston." "Tower." & "A.E.G."
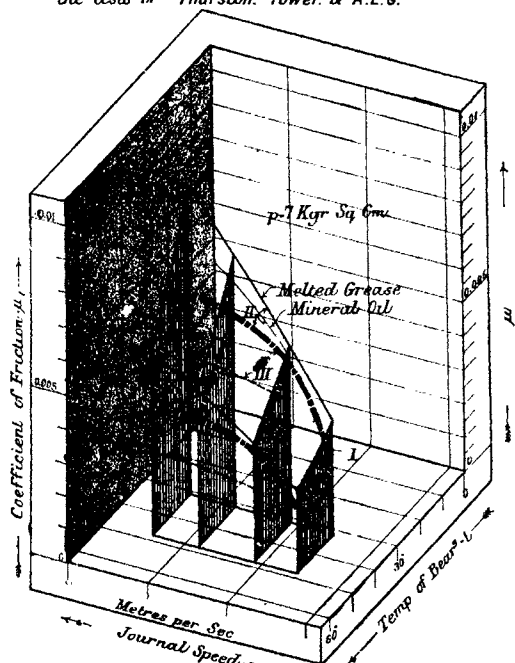
		JOURNAL	BUSHES.	OIL	LOAD ON
I	Thurston	Steel	Gun-Metal	Sperm Oil	Top & Lower Bush
II	Tower	Steel	Gun-Metal Dia.102. l.152.	Melted Grease Mineral Oil	Top Bush
III	A.E.G	Nickel Steel	Gun Metal Dia.260 l.110	Imperial 'O' Oil	Lower Bush

FIG. 32.

O. Lasche[1] has made an elaborate series of experiments on the friction and lubrication of motor bearings at journal speeds rising to nearly 4000 feet per minute, and at pressures up to 213 pounds per

[1] *Traction and Transmission*, Jan. 1903, p. 33. We are indebted to the proprietors of *Engineering* for the use of the blocks of figs. 32 and 33, borrowed from their paper.

square inch. Measurements of the friction were made under varying conditions of load, speed, temperature, fit of bearings, and method of applying the lubricant, the results generally confirming those obtained by Tower and Thurston. Measurements were also made of the work expended in overcoming friction, and of the dissipation of heat from bearings by conduction, radiation, and by the flow of oil between the friction surfaces.

As regards the influence of speed on the coefficient of friction, Lasche shows that the results obtained by Tower, Thurston, and in the above experiments, which were carried out for the Allgemeine Elektricitäts-Gesellschaft of Berlin, are in agreement with Stribeck, who found that above very low speeds and up to speeds of 2·5 metres per second (492 feet per minute) the frictional coefficient increases as the square root of the speed, as shown by Tower. *From 2·5 metres to 4·0 metres per second (788 feet per minute), however, the rate of increase was found to approach the fifth root of the speed, as found by Thurston, and at still higher speeds the influence of velocity was observed to gradually disappear, and above speeds of about 10 metres per second (1970 feet per minute), the friction coefficient became practically independent of the velocity.* The diagram (fig. 32) by Lasche graphically compares the results obtained by Tower, Thurston, and himself in so far as they cover the same experimental ground.

Osborne Reynolds concluded from his theoretical investigation of the friction of lubricated journals that if the viscosity of the lubricant remained constant the friction would increase proportionally to the speed. Owing, however, to the fact that the heat resulting from the viscous friction of the lubricant raises the temperature of the whole of the bearing above that of the atmosphere, and also locally raises the temperature of the oil film very considerably, the viscosity of the lubricant decreases with increasing speed, and consequently the friction increases at a less rapid rate than the speed. The extent to which the viscosity of any particular lubricant decreases with increase of temperature depends, of course, upon the nature of the oil, the rate at which it is supplied to the bearing, and the rate at which the bearing loses heat by radiation and conduction. Hence different observers, experimenting with different

WORK OF FRICTION REDUCED TO V·I M.PER SEC.
(1) ● DETERMINED BY FRICTION BALANCE.
(2) ○ DETERMINED BY CALORIMETER.
(3) ✱ DETERMINED WITH°MOTOR
(Shaft carefully balanced).

Temperature of Bearing in C.Deg.

FIG. 33.

oils and different machines, have obtained results which have not agreed absolutely. But the results given above no doubt express the facts approximately.
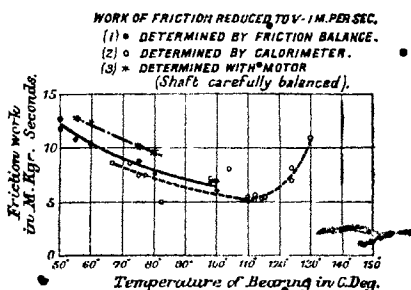
Diagram fig. 33, due to Lasche, shows the work required to over-come friction in relation to the bearing temperature. It is seen that the friction diminished with rise of temperature of the bearing and oil up to about 115° C., and that beyond this the friction increased again rapidly. The oil, in fact, became so thin that it ceased to lubricate.

Pressure of the Oil Film.—By means of a pressure gauge and of holes drilled in the brasses, Tower was able to measure the pressure of the oil film at various points of the surface.

Fig. 34 shows the exact curve of pressure calculated by Osborne Reynolds under conditions corresponding very closely with those in
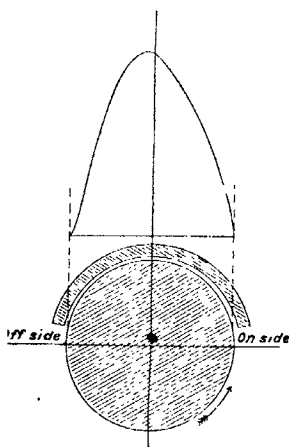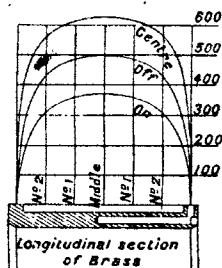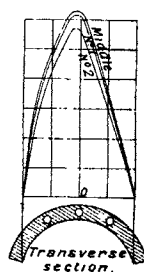
FIG. 34.   FIG. 35.   FIG. 36.

one of Tower's experiments, in which, by means of a pressure gauge, he actually measured the pressure of the oil at several points in the film. The observed pressures as plotted by Tower are shown in figs. 35 and 36. In this experiment, when the load was 100 lbs. per square inch, and the temperature was 70° F., the thickness of the film at various points must, according to Osborne Reynolds, have been as follows :—

         Radius of brass – radius of journal = ·00077 in.
         E_1F_1 (point of nearest approach) = ·000375 ,,
         Angle OJF   .   .   .   = 48°.

The possible motion of the fluid in a direction at right angles to that of the motion and parallel with the axis of the journal has not yet been referred to. In practice, the length of brasses is necessarily limited, and the oil can escape laterally. Such an escape

TABLE XII.—RESULTS OF TOWER'S EXPERIMENTS.

Temperature Fahr.	Relative Viscosities.	Coefficient of Friction for Speeds as below.							
		105 Feet per Min.	157 Feet per Min.	209 Feet per Min.	282 Feet per Min.	314 Feet per Min.	366 Feet per Min.	419 Feet per Min.	471 Feet per Min.
120°	35	·0024	·0029	·0035	·0040	·0044	·0047	·0051	·0054
110°	40	·0026	·0032	·0039	·0044	·0050	·0055	·0059	·0064
100°	48	·0029	·0037	·0045	·0051	·0058	·0065	·0071	·0077
90°	55	·0034	·0043	·0052	·0060	·0069	·0077	·0085	·0093
80°	65	·0040	·0052	·0063	·0073	·0083	·0093	·0102	·0112
70°	75	·0048	·0065	·0080	·0092	·0103	·0115	·0124	·0133
60°	89	·0059	·0084	·0103	·0119	·0130	·0140	·0148	·0156

will obviously prevent the pressure of the oil film from reaching its full height, except at considerable distances from the ends of the brass, and will cause it to fall to zero at the extreme ends.

The lubricant does not, therefore, all flow in a direction parallel with the direction of motion, except at the centre, but follows paths curved from the centre of the brass, some reaching the sides and escaping.

Tower measured the pressure at several points along the brass in a line through O (fig. 31), and found it to follow the curves of pressure shown in fig. 35, which correspond to those which might be expected to result from an escape of oil at the free ends.

Influence of Viscosity.—Just as, owing to the fact that the lubricating film can only thicken to an extent depending upon the difference between the radius of the brass and that of the journal, the frictional resistance is practically independent of the load, so *the friction of a cylindrical journal should be proportional to the viscosity of the lubricant.*

The effects of viscosity have been experimentally determined by Beauchamp Tower for various speeds above that at which the pressure film is fully formed. The lubricant used was lard oil, the viscosity of which was varied by heating the journal and brass. The viscosity of the lard oil used was not specified, but Goodman gives its probable comparative values at the temperatures stated.

Table XII. is taken from Tower's paper, with the addition of a column giving the comparative viscosities. The experimental results will be seen to be entirely in agreement with theory, the friction at each speed and temperature being as nearly proportional to the viscosity as can be expected when the experimental difficulties to be overcome are borne in mind. With increasing speed, however, the temperature of the oil film is raised more and more above that of the metallic surfaces, and the friction ceases to be proportional to the speed.

In the experiments on the pivot bearing it was pointed out that the slight disagreement between experiment and theory might be accounted for by the heating of the film. With parallel surfaces the friction varies only as the square root of the viscosity. No very marked effect was therefore to be anticipated from this heating, especially as the speeds were comparatively low. But in the case of a journal where the friction is proportional to the viscosity, the effect might be very marked. Indeed, there are grounds for believing that, as Osborne Reynolds contends, the reason why the resistance does not, in the case of a journal, increase at a rate proportional to the speed is that the rapid distortion which the oil suffers, heats it and lowers its viscosity.

Change of viscosity also has a considerable effect upon the carrying power. Table XIII., by Goodman, shows the effect which a change in the viscosity, brought about by rise of temperature, has upon the frictional resistance and carrying power of a journal, the speed being 7·8 feet per minute.

TABLE XIII.—OIL-BATH LUBRICATION.

Speed, 7·8 feet per minute.

Load in Lbs.	Temperature 40°.		30°.		20°.	
	μ_1.	F. Lbs.	μ_1.	F. Lbs.	μ_1.	F. Lbs.
50	·0061	·30	·0080	·40	·0084	·42
100	·0038	·38	·0041	·41	·0042	·42
150	·0027	·40	·0028	·42	·0028	·42
200	·0020	·40	·0021	·42	·0021	·42
250	**·0016**	**·40**	·0021	·52	·0019	·47
300	·0017	·51	·0017	·51	·0016	·48
350	·0021	1·22	**·0015**	**·52**	·0014	·49
400	·0029	1·16	·0016	·64	**·0013**	**·52**
450	·0042	1·89	·0019	·85	·0013	·58
500	·0189	9·45	·0044	2·20	·0029	1·45
550	·0515	28·33	·0126	6·93	·0764	42·03
560	·0562	31·48	·0142	7·95	·0937	52·47
580	·0724	42·00	·0253	14·68	·1086	63·00

The actual viscosities at the temperatures of the experiments were not determined. They must, however, have been greatest at the lower temperatures, and *vice versa*. Although the speed is low, there is, on the whole, a reduction of the friction as the temperature increases, when the loads are small, but not so marked a change as might be expected. It will also be noticed that *the greater the viscosity, the greater the load which the bearing will carry without undue friction resulting from the failure of the pressure film to form properly.* In this table the loads between which the coefficient of friction has a minimum value have been printed in heavy type.

The reduction in the frictional resistance which results from the lowering of the viscosity by the heating of the lubricating film is by no means advantageous, and accounts in a great measure for the failure of bearings to carry heavy loads at high speeds. The heating is most severe when the film is thinnest, *i.e.* at the point E_1F_1, fig. 30. Reduced viscosity at this point greatly lowers the carrying power of the brass. Again, if from any cause the bearing should become warm, mineral oils become very fluid and cease to lubricate properly.

Influence of the Area of Bearing Surface.—With parallel plane surfaces it was found that the friction does not increase much when the area is increased, for an increase of area brings about an increase in the *thickness* of the film. But here again a cylindrical form of bearing gives a different result, the frictional resistance being more nearly proportional to the area, owing to the fact that when the speed is moderately high the film has a fairly constant effective thickness under all loads.

TABLE XIV.—BATH LUBRICATION (GOODMAN).

LENGTH OF BRASS, 4 INCHES. SPEED. 121·9 FEET PER MIN.

Total Load in Lbs.	Width of Chord in contact, 2 in. Angle subtended 180°.		1·75 in. 122°.		1·5 in. 97°.		1·0 in. 60°.		·5 in. 29°.	
	μ.	F. Lbs.	μ.	F. Lbs.	μ.	F. Lbs.	μ.	F. Lbs.	μ.	F. Lbs.
50	·0441	2·20	·0458	2·29	·0418	2·09	·0210	1·05	·0126	·63
100	·0288	2·88	·0238	2·38	·0209	2·09	·0105	1·05	·0084	·84
150	·0192	2·88	·0160	2·40	·0140	2·10	·0070	1·05	·0056	·84
200	·0139	3·18	·0121	2·42	·0106	2·12	·0055	1·10	·0042	·84
250	·0128	3·20	·0097	2·42	·008?	2·12	·0044	1·10	·0034	·84
300	·0103	3·09	·0081	2·43	·0071	2·13	·0037	1·11	·0028	·84
350	·0085	2·97	·0070	2·45	·0061	2·13	·0033	1·15	·0024	·84
400	·0071	2·84	·0062	2·48	·0054	2·16	·0029	1·16	·0021	·84
450	·0062	2·79	·0055	2·47	·0049	2·20	·0028	1·26	·0019	·84
500	·0058	2·90	·0049	2·45	·0044	2·20	·0029	1·45	·0017	·84
550	·0051	2·85	·0045	2·47	·0040	2·20	·0027	1·48	·0015	·84
Mean	…	2·89	…	2·42	…	2·14	…	1·18	…	·82

Table XIV., giving the results of some experiments by Goodman, brings this out very clearly. The frictional resistance at different loads does not vary very much. On the other hand, the long narrow brass offers a very much smaller resistance to the motion of the journal than does the brass having a chord of contact measuring 2 inches. The area of the surfaces is in all cases proportional to the length of the arc of contact which is given for each size of brass. If the film were of even thickness throughout the length of the arc, the friction would be simply proportional to its length. The film, however, is much thicker on the 'on' side, where the lubricant enters, than it is nearer the centre of the brass. The resistance offered to the motion of the journal by those portions of the brass respectively near the 'on' and 'off' sides are, therefore, less than the friction near the middle of the bearing, and, as the brass is cut away at the sides, the thickness of the film is also very slightly reduced. The reduction of the resistance is, therefore, not quite proportional to the reduction of the area, as will be seen by comparing the lengths of the arcs with the mean frictional resistances. A closer approximation of the obtained results with theory cannot be expected, as everything depends upon the curvature of the surfaces remaining unaltered during the experiments.

Influence of the Method of Lubrication.—As stated on p. 56 the method of lubrication has a much greater influence on the friction at high than at low speeds. The results given in Table XV. by Goodman illustrate this.

TABLE XV.—INFLUENCE OF METHOD OF LUBRICATION AND CONTACT AREA UPON FRICTIONAL RESISTANCE.

Length of Bearing, 4 Inches ; Speed, 122 Feet per Min.

Method of Lubrication.	Width in Inches of Chord of Bearing Surface.				
	2·0	1·75	1·5	1·0	0·5
	Frictional Resistance in Lbs.				
Oil-bath, . .	2·89	2·42	2·14	1·18	0·82
Saturated pad, . .	4·47	3·98	2·49	2·10	1·06
Oily pad, . . .	7·97	6·62	5·80	3·80	2·70

Bath or 'perfect' lubrication is obtained by allowing the under side of the journal to dip into a bath of the lubricant. In this way the journal picks up and throws against the brass a thick film of oil, and the result is 'perfect lubrication,' *i.e.* the thickest film is secured which the bearing can automatically maintain.

Pad lubrication is obtained by pressing a woollen or felt pad soaked with the lubricant against the journal. When the pad rest in a bath of the lubricant and is kept thoroughly soaked, the result obtained are not greatly inferior to those given by the bath. When however, the supply of oil to the pad is deficient, the difference i marked, as will be seen from the results given in the table.

Alternating Pressures.—In some cases the loads upon bearings are by no means constant, for the faces often alternately approach and recede from each other. When this is the case, and the alterna tion is very rapid, the bearing will carry a very great weight, for a each alternation the pressure is completely relieved, and the oi 'trapped' cannot be expelled during the short time the load rests on the bearing. The large ends of connecting rods may be instanced as cases in point. Here, although the pin is rapidly rotating in the brasses, the load frequently reaches several tons per square inch. On the small end brasses the load may be even greater, for the angula movement of the brass on the pin is only small. The reason why the lubricant cannot escape whilst the pressure lasts is doubtless that the volume of oil which can be 'squeezed' out by any particular load is proportional to the cube of the thickness of the film.

Wear of Cylindrical Bearing Brasses.—To obtain a low coefficien of friction when the bearing surfaces are cylindrical in form, the radius of the journal must be rather smaller than that of the brass so as to leave space for a film of the lubricant to insinuate itsel between the surfaces. When the bearings have been newly and accurately fitted, together, the friction is generally high, but afte: they have been at work for some time, the resistance is found t have largely decreased. This results mainly from the altered shape of the brasses consequent on wear. The exact nature of the wear which takes place in rubbing surfaces is, therefore, of the utmos importance, for upon it depends very largely the frictional resistance of the bearing. Unfortunately, this aspect of the question has only received a very small amount of attention. Indeed, until more evidence is forthcoming concerning the results of wear, we have no guarantee that the friction is really independent of the load ; for there is every reason to believe that upon the load largely depends the shape the surfaces assume from wear. Thus, although whei the surfaces have arrived at a certain shape, rapid changes of load do not alter the frictional resistance, it is not unlikely that for each load, if it act for any length of time, there is a different curve o brass, and therefore a different frictional resistance.

' .As at high-speeds the oil film is practically continuous and keeps the surfaces quite apart, such wear as then occurs must result from the intrusion of solid particles rather larger in diameter than the thickness of the lubricating film. But, doubtless, the chief wear takes place at low speeds when the surfaces are in contact. Actua abrasion then occurs.

When moving very slowly, the brass actually touches the journa

at E_1F (fig. 30), or even on the 'on' side of O (fig. 31), but at ordinary speeds the liquid is *wedged* between the surfaces and keeps them apart on this side. Thus the wear is almost wholly on the 'off' side, where, except at considerable speeds, the surfaces touch, and the brasses when not very narrow are worn to a larger radius than that of the journal. When the journal is not in motion, the point of contact will be at O ; consequently, as the speed changes, the position of abrasion will also change. The action is the same whether the brass be lubricated by a siphon supplying oil to the crown of the bearing, or by a pad beneath the journal. However, when the chord of the arc covered by the brass is small, the wear tends to become more evenly distributed over the whole bearing surface. Even then the wear tends to make the radius of the brass larger than that of the journal, and thus renders efficient lubrication possible.

In the case of railway journals and brasses, the wear is sometimes on one side of the brass and sometimes on the other, according as the direction of motion of the vehicle changes ; but when the shaft or journal always rotates in the same direction, the wear is always on the same side. This one-sided wear often disturbs the adjustment of mechanical oil-testing machines, and effects arising from this cause should always be looked for.

Air as a Lubricant.—The action of a lubricant in a journal bearing has been ingeniously illustrated in a machine designed by Prof. A. Kingsbury.[1] The following description is taken from the *Chemical Trade Journal*, vol. xxvi. p. 232 :—

The machine consists of a steel piston or short shaft to be rotated, and a cast-iron ring or cylinder which acts as a bearing for the shaft, the whole being supported on rollers mounted on a suitable frame. The shaft weighs $50\frac{1}{2}$ lbs., is $6\frac{1}{4}$ inches long and 6 inches in diameter, and its weight constitutes the total downward pressure on the bearing. The diameter of the cylinder is slightly less than $\frac{1}{2000}$ inch larger than the shaft—a fairly loose fit. Both cylinder and shaft are ground exactly parallel.

The cylinder is set horizontally, the shaft inserted (both being perfectly clean and dry), and rotated with the hand by the handle at the end. It can be turned with difficulty at first, and the harsh, grating sound of metal rubbing on metal will be heard. With an increase of speed, however, this grating ceases and the force required to turn the shaft is materially decreased until, after a few revolutions, the shaft becomes entirely free from the cylinder and rotates on the film of air between. Set rotating at, say, 500 revolutions per minute, it will continue to rotate four or five minutes. If allowed to run, the speed gradually decreases from the start until, suddenly, the piston breaks through the intervening layer of air, and a few more revolutions suffice to bring it to a sudden stop. If a more conclusive proof is required that the shaft is entirely separated from the cylinder, an electric bell may be included in a circuit of which the shaft is made

[1] *Jour. Amer. Soc. Naval Engineers,* 1897.

one terminal and the cylinder the other, when it will be found that the bell is silent so long as the shaft rotates at any considerable speed. It is interesting to note that with this machine Kingsbury found the minimum coefficient of friction of the journal lubricated by air to be 0·00075, which is nearly the same minimum coefficient as he observed with oil as a lubricant when the lubricating film was perfect (see p. 364).

Ball and Roller Bearings.—Of late years ball and roller bearings have come into very extensive use, having been found very suitable for slow stopping trains, motor-cars, cycles, dynamos, and other machines the bearings of which have to carry moderate loads.

One of the early forms of ball-bearing known as the 'Rudge' was experimented upon by Goodman. The results of his experiments are given in Tables XVI. and XVII. The results with the white 'neutral'

TABLE XVI.—RUDGE BALL BEARING.   WHITE 'NEUTRAL' OIL.

Load in Lbs.	Speed, 19 Revolutions per Minute.		Speed, 157 Revolutions per Minute.		Speed, 350 Revolutions per Minute.	
	Coefficient of Friction.	Frictional Resistance, Lbs.	Coefficient of Friction.	Frictional Resistance, Lbs.	Coefficient of Friction.	Frictional Resistance, Lbs.
10	·0060	·06	·0105	·10	·0105	·10
20	·0045	·09	·0067	·13	·0120	·24
30	·0050	·15	·0050	·15	·0110	·33
40	·0052	·21	·0052	·21	·0097	·39
50	·0054	·27	·0054	.27	·0090	·45
60	·0050	·30	·0055	·33	·0075	·45
70	·0049	·34	·0054	·38	·0068	·47
80	·0048	·38	·0062	·49	·0060	·48
90	·0050	·45	·0068	·61	·0060	·54
100	·0058	·58	·0069	69	·0057	·57
110	·0054	·59	·0065	·71	·0060	·66
120	·0055	·66	·0075	·90	·0057	·68
130	·0058	·75	·0078	1·01	·0062	·81
140	·0056	·78	·0077	1·08	·0060	·84
150	·0060	·90	·0083	1·24	·0062	·93
160	·0075	1·20	·0081	1·29	·0058	·93
170	·0079	1·31	·0078	1·33	·0055	·93
180	·0079	1·42	·0078	1·40	·0053	·95
190	·0087	1·65	·0076	1·44	·0054·	1·03
200	·0090	1·80	·0081	1·62	·0060	1·20
Mean	·0060	...	·0070	...	·0071	...

oil are rather irregular, but their average clearly shows that, as with the pale American oil the coefficient of friction varies very little with

moderate loads ; the frictional resistance, therefore, varies almost directly as the load.

To ascertain the effects of viscosity, the bearing was heated by a Bunsen gas-burner from 20° to 60° C., but no difference could be detected in the friction. The experiment was repeated with different lubricants, loads, and velocities, with the same negative results. In the case of ball bearings, a lubricant only alters the area in contact over which slip takes place, and although it does not decrease the friction it prevents undue wear, and prolongs the life of the bearing.

TABLE XVII.—RUDGE BALL BEARING. PALE AMERICAN OIL.

Load, Lbs.	Speed, 19 Revolutions per Minute.		Speed, 157 Revolutions per Minute.	
	Coefficient of Friction.	Frictional Resistance, Lbs.	Coefficient of Friction.	Frictional Resistance. Lbs.
10	·0075	·07	·0060	·06
20	·0075	·15	·0075	·15
40	·0071	·28	·0075	·30
68	·0070	·42	·0075	·45
80	·0071	·57	·0071	·57
100	·0073	·73	·0072	·72
120	·0071	·85	·0069	·83
140	·0072	1·01	·0067	·94
160	·0072	1·15	·0066	1·06
180	·0072	1·30	·0066	1·19
200	·0073	1·46	·0066	1·32
Mean	·0072	...	·0068	...

From these experiments the following laws, therefore, are deducible :—

1. The coefficient of friction is nearly constant for all ordinary loads; hence, unlike lubricated cylindrical bearings, the frictional resistance varies directly as the load.

2. The friction is unaffected by change of temperature, and therefore by moderate changes in the viscosity of the lubricant.

The coefficient of friction of ball bearings at high speeds is rather higher than that of ordinary bearings when bath or saturated pad lubrication is used, but is less than the friction of ordinary brasses when the latter are lubricated by less perfect methods. · The friction of ball and roller bearings is also small at very low speeds and with small loads, much smaller indeed than could be obtained with ordinary bearings at such speeds, even by bath lubrication.

Owing to their small frictional resistance roller bearings have lately

been tried and have given very favourable results on electric railways, trams, and motor-cars.

Bailey Marshall[1] states that on railway vehicles the starting effort is, in many cases, as low as 3 lbs. per ton, a figure which compares favourably with the frictional resistances of ordinary bearings at high speeds when well lubricated ; but it seems doubtful whether roller bearings will, when used for such high speeds, give better results than brasses of the ordinary design.

In the case of ball bearings the design should be such that the lubricant used can escape readily on each side of the balls as they roll in their races ; with rollers, however, the lubricant must be pushed along in front of them. On this account, the viscosity of the lubricant used must have an appreciable effect upon the friction in the latter case.

In a paper read before the Tramways and Light Railways Association in October 1905, by Thomas W. How, the author deals with the requirements of a satisfactory roller bearing for heavy and light loads, the efficiency of which largely depends upon true parallelism, proper spacing, and proportionate diameter, length, and hardness of the rollers. He gives examples of various contrivances for spacing the rollers, regarding the 'Empire' floating cage as the most satisfactory, owing to its simplicity and easy adjustment ; and he advocates the employment of solid rollers of special steel rather than of spiral or hollow ones, or rollers threaded on spindles. The want of success of earlier experiments made with roller bearings is attributed to causes now well understood and avoided, such as excessive rigidity and improper load adjustment, these being now obviated by means of swivel seatings, so that the alignment of the load is evenly distributed, and several examples are given of the successful application of roller bearings to railway and tramway stock.

The relative friction of ball, roller, and plain bearings was investigated some years ago in Germany by Stribeck, a summary of whose chief results is given in the paper by H. Hess referred to in Chapter X., p. 426, where further information on the subject of ball and roller bearings will be found.

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[1] *Roller Bearings* (pamphlet).   London, 1897.

CHAPTER V.

LUBRICANTS.

LUBRICANTS are, with few exceptions, fluid or semi-fluid substances, capable of forming and maintaining between friction surfaces films of sufficient thickness to keep the surfaces apart, thus abolishing the solid friction and substituting for it the much less considerable friction of the fluid itself. The substances which possess in the highest degree the necessary properties belong to the class of bodies known as fixed oils and fats. Until the latter half of the present century lubricating oils were almost exclusively derived from the animal and vegetable kingdoms, though cart-grease had been prepared from petroleum in Galicia from a very early period (*Redwood*), while early in the present century the advantages of petroleum as a lubricant free from 'gumming' properties were sufficiently well known to lead to its more general use in places where it could be obtained. The rise and development of the modern petroleum, and shale oil industries, stimulated by the increased demand for lubricants due to the introduction of railways and the extended use of machinery, has led to the production of immense quantities of lubricating oils, which, besides largely augmenting the general supply, have, owing to their cheapness and other advantages, displaced to a great extent the older lubricants. We shall, therefore, commence with a description of this class of oils, which, being derived from mineral sources, have received the name of

A.—MINERAL OILS.

I. Sources.

(*a*) **Petroleum.**—Crude petroleum is a highly complex liquid product which is found very abundantly in various parts of the world either issuing naturally from the ground or reached by boring. Its occurrence is not limited to any particular country, continent, or

geological formation, but by far the greater volume is obtained in the United States of America and in the neighbourhood of Baku in the Caucasus (Russia).

The following tabular statement prepared by Redwood and East-lake gives the world's production of crude petroleum in imperial gallons for the year 1904 :—

WORLD'S PRODUCTION OF PETROLEUM FOR 1904, IN IMPERIAL GALLONS.

Country.		Quantity.	Percentage of Total.
UNITED STATES—			
Appalachian field,[1] .	1,098,992,039		
California, . .	1,037,439,620		
Lima-Indiana field,	863,879,481		
Texas, . . .	778,231,491		
Kansas, . .	148,735,609		
Louisiana, .	102,920,841		
Indian and Oklahoma			
Territories . .	47,822,787		
Colorado, . .	7,556,789		
Wyoming, . .	403,858		
Missouri,[2] . .	89,996		
	4,096,072,511	4,096,072,511	53·5491
RUSSIA—			
Baku field, .	2,554,034,653		
Grozni field, .	162,380,753		
	2,716,415,406	2,716,415,406	35·5125
EASTERN ARCHIPELAGO—			
Sumatra,[3] .	186,322,815		
Java,[3] .	30,381,990		
Borneo,[3] .	63,507,213		
	280,212,018	280,212,018	3·6632
GALICIA, ...		215,796,231	2·8211
ROUMANIA, ...		129,829,004	1·6972
Carry forward, . .		7,438,325,170	97·2431

[1] The Appalachian field comprises New York, Pennsylvania, West Virginia, South-eastern Ohio, Kentucky, and Tennessee.
[2] Includes the production of Michigan.
[3] Estimated.

WORLD'S PRODUCTION OF PETROLEUM FOR 1904, IN IMPERIAL GALLONS—
continued.

Country.		Quantity.	Percentage of Total.
Brought forward, . .	7,438,325,170		97·2431
INDIA—			
Burma, . . 115,903,804			
Assam, . . . 2,585,920			
Punjab, . . 1,658			
118,491,382	118,491,382		1·5490
JAPAN, . . .	...	49,606,579	·6485
GERMANY—			
Hanover, . 16,556,691			
Elsass, . . . 5,392,988			
21,949,679	21,949,679		·2869
CANADA, . . .	...	17,237,220	·2253
PERU, . . .	...	1,732,848	·0226
ITALY, . .	...	976,371	·0127
HUNGARY,[1] . .	...	857,351	·0112
Total . .		7,649,176,600	99·9993

[1] Estimated.

The most important commercial product obtained from the crude petroleum of the older oilfields of the United States is illuminating oil or kerosene, only a comparatively small percentage of the raw material being represented by lubricating oil, but the crude oils of California and Texas are of lower volatility and are largely used as liquid fuel. For the year 1904 the total exports of illuminating oil from the United States amounted to 761,358,155 American gallons, and of lubricating oil and paraffin to 89,688,123 American gallons. The exports of illuminating oil from the United States to the United Kingdom for the fiscal year 1904 amounted to 165,248,727 American gallons, and of lubricating oils to 33,890,901 American gallons.

Russian petroleum yields a comparatively small percentage of illuminating oil, the residuum or ostatki, so largely used as fuel, representing about two-thirds of the crude oil. A small portion of this ostatki is distilled, and lubricating oils are thus obtained, but the Russian petroleum business is primarily a liquid fuel industry.

Crude *American* petroleum varies very much in character in different districts, ranging in colour from pale amber to dark greenish-or brownish-black, and in specific gravity from about 0·78 to 0·94 (*Höfer*). Some oils are highly limpid, and are composed for the most part of the lighter hydrocarbons suitable for burning in lamps ; others contain a large proportion of lubricating hydrocarbons. A few crude oils can be used for lubricating almost without treatment (see ' Natural Oils '). Most of the crude petroleum obtained in the United States is distilled for illuminating oil and naphtha, only the still residues (' residuum ') being worked up into lubricating oils and paraffin wax ; but there are some heavy oils which, being chiefly valuable for the manufacture of lubricating oil, are treated separately. Researches too numerous to mention have shown that American petroleum is composed mainly of hydrocarbons of the paraffin series, C_nH_{2n+2}, with smaller quantities of naphthenes, and of benzene and its derivatives. Traces of sulphur are met with in most petroleum, also oxygenated bodies of acid and phenolic character, and variable traces of mineral matter.

Canadian petroleum resembles the oil of Lima (Ohio) in having an offensive odour and containing a, notable proportion of sulphur. The production is comparatively small, and the oil is refined for home consumption.

Crude *Caucasian* petroleum is, in many respects, specially interesting : in the antiquity of historical references to it ; in the comparatively small area within which the supply is obtained ; in the extraordinary productiveness of the wells, and in the peculiar character of the hydrocarbons of which the oil is mainly composed. According to the researches of Markownikoff and Ogloblin, and others, at least 80 per cent. of crude Baku petroleum consists of hydrocarbons of the naphthene series, C_nH_{2n}, isomeric with the olefines, but differing from them in not combining directly with bromine. Naphthenes are closed-chain hydrocarbons, also known as polymethylenes, one of the most important being hexamethylene or hexhydrobenzene, C_6H_{12}, which has been obtained in large quantity from Russian and in small quantity from American petroleum.[1] Russian petroleum also contains paraffins and a considerable quantity of aromatic hydrocarbons.

Caucasian petroleum is more uniform in composition than the American product. It usually ranges in specific gravity from 0·850 to 0·875 ; yields a larger proportion of lubricating oil, less, illuminating oil and less naphtha than American petroleum, but no paraffin wax. Owing to the almost entire absence of solid hydrocarbons, Russian lubricating oils will bear exposure to a much lower temperature than American oils without solidifying.

Galician-petroleum is stated by Redwood to have been collected in a primitive fashion and used as a cart-grease from very early times. The Galician oilfields are very extensive, and produce oils of very

[1] Young, *Jour. Chem. Soc.*, 1898, Transactions, p. 905.

varied character, both light and heavy. Crude Galician petroleum is composed chiefly of hydrocarbons of the paraffin series. According to Dr. Young, it contains more naphthenes and aromatic hydrocarbons than American, but probably less than Russian petroleum. It yields 55 to 65 per cent. of lamp oil, and from 30 to 40 per cent. of residuum from which lubricating oils are obtained.[1]

From the tabular statement already referred to it will be seen that the Eastern Archipelago now occupies an important position among the sources of the world's supplies of petroleum. Much of the crude oil of *Sumatra* contains an unusually large proportion of the more volatile hydrocarbons, which are separated by fractional distillation as petroleum spirit, whilst that of *Java* is characterized by the presence of solid hydrocarbons (paraffin) in large quantity. The crude petroleum of *Borneo* has in the past been looked upon as a heavy oil, chiefly suited for use as fuel, but recently a large production has been obtained at Kotei of oils yielding the usual commercial products, and the oil from some of the wells contains much solid paraffin.

The petroleum of *Upper Burma* has long had a high reputation as a source of lubricating oil, 'Rangoon oil' having been originally made from it. The petroleum industry of Burma has for some time past exhibited rapid growth, and the markets of India are largely supplied with the products. The crude oil yields only a moderate quantity of illuminating oil, the lubricating oils and solid paraffin being important products.

The production of *Roumania* also exhibits rapid progression, and will no doubt assume still greater importance, in view of the character of the oil-bearing territory and its geographical position.

(*b*) **Shale.**—Although by far the greater proportion of the lubricating oil of commerce is now obtained from petroleum, it is of interest to remember that shale oils were the first to be produced on a large scale even in America. Prior to the boring of Drake's well in 1859, which was the commencement of the United States petroleum industry, a number of works were established in that country for the production of oil from coal and shale, and Boghead cannel was even imported from Scotland for the purpose ; these factories, which worked under licence from Dr. James Young, the founder of the Scottish Shale Oil Industry, were subsequently converted into petroleum refineries (*Redwood*). Young's first patent for obtaining paraffin oil from bituminous coal was taken out in 1850, and the mineral which he used was Boghead cannel, a rich bituminous mineral yielding by distillation from 120 to 130 gallons of oil per ton. The supply of this mineral soon became exhausted, and since then the Scotch oil has been produced from the bituminous shales of the coal measures. The manufacture of paraffin oil from shale at the works of

[1] For an interesting and very complete account of the Galician petroleum and ozokerite industries, see a paper by Redwood, *Jour. Soc. Chem. Ind.*, 1892 pp. 93–119.

the Broxburn Oil Company, has been described by D. R. Steuart (*Jour. Soc. Chem. Ind.*, 1889, pp. 100–109). The shale is a dark grey or black mineral with a laminated or horny fracture. The greater proportion (73 to 80 per cent.) consists of *mineral matter*; the remainder (27 to 20 per cent.) is *bitumen*, composed chiefly of carbon and hydrogen, with some nitrogen and sulphur. When the shale is heated to a very low red heat in retorts, this bitumen undergoes *destructive distillation*, splitting up into water, ammonia, gas, and oil. Each ton of shale distilled at Broxburn yields on an average 30 gallons of crude oil, 65 gallons of ammoniacal water, and nearly 2000 cubic feet of permanent gas, which is used for lighting the works and for fuel.

(*c*) **Crude Shale Oil** is dark green in colour, has a specific gravity of 0·860 to 0·890, and is semi-solid at ordinary temperatures owing to the large quantity of solid paraffins ('paraffin wax') contained in it. When warmed to 90° or 100° F., the oil becomes quite fluid. Chemically, it is composed chiefly of hydrocarbons of the paraffin and olefine series, the latter predominating in the fractions used as lubricating oil. Naphthenes and aromatic hydrocarbons are also present in large quantity (Heusler, *Jour. Chem. Soc.*, 1898, Abstracts, Part I. p. 101).

II. Manufacture.

The manufacture of lubricating oils from crude petroleum and shale oil is a branch of a very extensive industry. The great variety of hydrocarbons of which the crude oils are composed affords material for the manufacture of numerous products. The lightest and most volatile hydrocarbons compose **Crude Naphtha,** from which rhigolene, gasoline, benzoline, petrol, motor spirit, and similar products are obtained. These liquids, which are devoid of all lubricating property, form highly volatile and inflammable 'spirits,' used for freezing, driving motors, making air gas, carburetting coal gas, and for solvent and other purposes. Hydrocarbons of higher boiling-point and specific gravity, which are still too fluid and volatile to be used for lubricating, compose the **Illuminating Oils** of commerce known as kerosene, petroleum, paraffin oil, etc. The heaviest and least volatile hydrocarbons are alone used for the manufacture of **Lubricating Oils, Paraffin Wax,** and **Vaseline.** The refiner's business is to separate the various products from the crude oil and purify them for use, and this he does by distillation and chemical treatment.

The value of distillation depends upon the fact that the different constituents of the crude oil boil and volatilise at different temperatures, the naphtha coming over first, then the illuminating oils, then some 'intermediate' oils used for gas-making, or destructively distilled so as to increase the quantity of illuminating oil (see below), leaving the heaviest hydrocarbons, unless the distillation is continued to dryness, as a residue or **Residuum** in the still. By separate frac-

tional distillation, the naphtha is subsequently split up into gasoline, benzoline, etc., the crude illuminating oil into products of different specific gravities and flashing-points, and the residuum into lubricating oils of various grades and paraffin wax.

In practice, however, the distillation, especially of the heavier fractions, is never a simple process of separation, as is proved by the fact that products are found in the distillates which do not exist in the original liquid. During the distillation the heavier hydrocarbon vapours partly condense on the upper and cooler part of the still and fall back into the boiling liquid, while, in distilling the heavy oil, the boiling has to be very vigorous to keep up the stream of vapour issuing from the retort, which necessitates a strong fire and a high temperature at the bottom and sides of the retort.[1] The prolonged and excessive heating to which the heavier hydrocarbons are thus subjected gradually splits them up, partly into permanent gases (marsh gas and hydrogen), partly into liquid hydrocarbons of lower boiling-point and viscosity, which distil over, and partly into tarry products which remain in the still. It has been found, in fact, that by setting the still so that the upper part is kept cool, and conducting the distillation slowly in order to promote condensation, or by distilling under increased pressure and so raising the boiling temperature of the liquid, the **destructive distillation** or 'cracking' of the heavier hydrocarbons may be promoted to such an extent as to largely increase the natural yield of illuminating oil at the expense of the heavier fractions. Large quantities of crude petroleum, in which the residuum is not of special value for the preparation of lubricants, are distilled in this way in the United States, the illuminating distillate being increased from a normal proportion of about 50 per cent. to as much as 70 or 75 per cent., and the residuum reduced to as little as 6 per cent. According to Steuart, the hydrocarbons of petroleum are more readily split up than those of shale oil, and in Scotland cracking for the production of illuminating oil is not practised. A certain amount of destructive distillation is, however, necessary for the production of the paraffin wax which is such an important product of the shale oil industry. The quantity of crystalline wax obtainable from crude shale oil by direct freezing is much less than is obtained by freezing the distillates resulting from the distillation of the oil in such a way as to cause partially destructive changes.

Destructive distillation which is so valuable in increasing the yield of illuminating oil and in the production of paraffin wax has been found to be most detrimental to the quality of the lubricating oil, reducing the viscosity, lowering the boiling- and flashing-points, and

[1] Steuart (*Jour. Soc. Chem. Ind.*, viii. 106) has pointed out that whilst water in being converted into steam increases in volume 1700 times, burning oil increases less than 200 times, and heavy oil less than 100 times. In distilling the heavy oil a great deal has, therefore, to be converted into vapour before enough is formed to reach the point of exit from the still, and as the specific heat of the vapour is low, it is easily condensed and falls back into the boiling liquid.

tending generally to the production of an inferior product. When, therefore, the primary object of the distillation is to obtain the lubricating oil with its viscosity, chemical stability, and other valuable qualities unimpaired, every care is taken to reduce the amount of *destructive* distillation to a minimum. With this object the **Steam Refining Process** was introduced about 1870. In this process, which is largely used in the manufacture of lubricating oils from crude petroleum and petroleum residuum, a current of steam superheated to the required temperature (varying from 150° to 300° C.) is blown through the oil during the distillation, by which means the hydrocarbon vapours, instead of remaining in the still and undergoing decomposition, are swept rapidly forward into the condensing worm. Further improvements have been effected, especially in the distillation of the heavier hydrocarbons, such as form vaseline and cylinder oils, by conducting the distillation in a partial **vacuum**, maintained by means of an exhaust ejector or other appliance connected to the end of the condensing worm. The boiling temperatures of the hydrocarbons are thus lowered, and the rapidity of the distillation is much increased.

In addition to these modifications in the process of distillation, the plant has also been improved. The thick-walled cast-iron stills at first employed, in which the proper regulation of the temperature was impossible, have given place to stills of wrought iron or steel ; the vertical form of still has been abandoned in favour of the horizontal, so as to increase the evaporating surface, and the stills are provided with low domes or short goose necks in order to still further diminish the distance traversed by the heated vapours. The result of all these improvements in the plant and processes has been a great improvement in the quality of mineral lubricating oils, to which must be attributed the rapid manner in which their use has extended during recent years.

The lubricating oils manufactured from crude petroleum in the United States are of three kinds, viz. :—*natural, reduced*, and *distilled* oils.

(*a*) **Natural Oils.**—A limited quantity of crude petroleum is found in the United States in which the proportion of lubricating hydrocarbons is so large that the crude oil only needs purification from suspended and tarry impurities by settling, straining, or filtering through charcoal, in order to render it fit for use. Lubricating oils obtained in this way are known as 'natural oils,' but very little oil of this description is now produced.

(*b*) **Reduced Oils.**—Crude petroleum rich in lubricating oil, but too fluid for use as a lubricant without treatment, is carefully distilled with steam or *in vacuo*, so as to avoid cracking, until the lighter hydrocarbons have been driven off. The distillation is then stopped, and the dark-coloured oil remaining in the still, reduced in volume but increased in viscosity, is known as 'reduced oil.' Such oils have considerable lubricating value, and are largely used on railways and

for heavy machinery. The chief objection to them is the tarry matter which they contain, which stains the machinery and paint, and interferes with the free siphoning of the oil. In the manufacture of *cylinder oil*, suitable descriptions of petroleum are carefully reduced at as low a temperature as possible, *in vacuo*; and for *filtered oil* the highly viscous residues thus obtained are repeatedly filtered through animal charcoal kept sufficiently warm to maintain the oil fluid, until the required degree of transparency is obtained. The reducing process is not always carried out in stills; the lighter hydrocarbons are sometimes evaporated by exposing the oil to the rays of the sun in shallow tanks containing water warmed by steam coils, the oil floating on and depositing its suspended impurities in the water. This process is known as 'sunning,' and the product as 'sunned oil.'[1]

. (*c*) **Distilled Oils.** —These oils are obtained from residuum. Those produced from American petroleum usually contain paraffin wax, and are known as '*paraffin oils*.' The Russian oils contain little or no paraffin. Distilled oils usually undergo treatment with acid and alkali by which they are partially decolorized and made transparent; in this way the '*pale oils*' are produced.

Residuum, as already described, is the tarry residue remaining in the crude-oil stills after the naphtha and illuminating oils have been distilled over with more or less cracking. As a rule, the distillation of the crude oil is stopped at this stage, the residuum is withdrawn from the still and, after standing for some time to allow the fine particles of coke contained in it to settle out, is transferred to special stills called 'tar-stills,' in which the distillation for lubricating oils is conducted with superheated steam, or *in vacuo*, generally in separate factories devoted to the manufacture of lubricating oil. The residuum obtained in the United States is very different, both in quantity and in quality, from the Russian product. By cracking, the yield of residuum from Pennsylvanian petroleum is reduced to as little as 5 to 10 per cent., whilst from the crude oil distilled at Baku at least 60 per cent. of residuum is obtained. This difference in the yield is not entirely due to the different character of the crude oil. Crude Pennsylvanian oil distilled without cracking will give from 20 to 30 per cent. of lubricating oil. and correspondingly less illuminating oil. At Baku, the residuum called by the Russians '*ostatki*,' and by the Tartars '*mazut*,' is in great demand for fuel, and there is not the same inducement to reduce the yield by cracking as in the United States.

. American residuum contains a variable proportion of solid hydrocarbons, and varies accordingly both in consistency and in specific gravity; it is the source of all the paraffin wax obtained in the United States. On the other hand, the Russian ostatki produced at Baku is a more fluid oil having a uniform specific gravity of 0·90 to 0·91, and containing so little solid hydrocarbons as to yield practically no paraffin wax.[2] Lubricating oil of a kind has been made in

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[1] A sunning process is also used in the manufacture of 'bloomless' oil (see p. 98)
[2] Engler, *Jour. Soc. Chem. Ind.*, 1886, p. 477.

the United States by simply filtering the residuum through steam-heated filters, but the unstable character of the product and the accompanying tarry matters unfit it for any but the roughest purposes. Russian residuum is similarly employed, after separation of water and treatment with sulphuric acid. But the usual method is to refine the oil by distillation with superheated steam. In the United States the distillation is carried to dryness. The first 20 to 25 per cent. of the distillate is a very fluid oil of about 0·834 sp. gr., which is either returned to the crude oil tank or is refined as a special high flash-point burning oil. The oil that follows is lubricating oil, and contains the paraffin wax; it is either collected all together or in separate fractions. Just at the end of the process, when the bottom of the still is red hot, a thick resinous product of light yellow colour and nearly solid consistency distils over, which is used as a lubricant for the necks of rolls,[1] or, according to Sadtler, is added to paraffin oils to increase the density and lower the cold-test. About 12 per cent. of coke remains in the retort, which is used for the manufacture of electric light carbons. The paraffin oil, if collected all together, is washed first with acid and then with alkali and is then reduced in temperature, which causes the paraffin to crystallize. The semi-solid mass is pumped into filter-presses, and the solid portion afterwards subjected to hydraulic pressure, the solid crystalline cake which remains being converted into refined paraffin wax. The fluid oil which drains from the presses is carefully redistilled and collected in separate fractions, yielding a variety of lubricating oils ranging in density and viscosity from the lightest and thinnest spindle oil to heavy machine oil and even cylinder oil, though cylinder oils are not usually made from residuum. If the paraffin oil, instead of being collected all together, is fractionated at the first distillation, then those fractions which contain the wax are separately treated for its recovery. Thus, according to Redwood, the second fraction following the oil of 0·834 sp. gr. (see above) may be collected so as to have a sp. gr. of 0·860-0·870, and may amount to 25 per cent. of the original residuum. This fraction may be subdivided by redistillation, or may be made into '*Neutral*' or '*Bloomless*' oil by cooling to separate the paraffin, filtering through bone-black to remove colour and odour, and exposing to the sun and air in shallow tanks, or treating with nitric acid or nitro-naphthalene or in other ways to remove fluorescence or 'bloom.' 'Neutral oil' has a very low viscosity, and is largely used for the adulteration of animal and vegetable oils, for which reason it is debloomed so as to remove the fluorescence which would betray its presence. The distillate following the neutral oil is the 'stock' for engine oil, and the percentage is determined (with a corresponding inverse variation in the proportion of the second fraction) by the use to which the product is to be put. For heavy machine oil the proportion is reduced, so that a distillate of sp. gr. 0·928 to 0·933 may be obtained, and

[1] *Jour. Soc. Chem. Ind.*, 1892, p. 142.

after the paraffin has been separated the viscosity is sometimes still further increased by distilling off some of the more volatile constituents by means of superheated steam and filtering the 'reduced' oil through charcoal.

Previous to the chemical treatment of the lubricating oil distillates, they are freed from mechanically mixed water by settling, and the last traces of moisture are got rid of by heating the oil in tanks fitted with steam coils. The dried oil is then thoroughly agitated with concentrated sulphuric acid, the proportion of acid varying from 4 to 12 per cent., according to the strength of the acid and the amount of impurity in the oil. After thorough settling, the clear oil is drawn off, agitated with a solution of caustic soda, and again allowed to settle; it is then well washed with warm water, allowed to rest until clear, and finally dried by being heated in shallow pans provided with steam coils until the oil is bright. Sometimes the oil after being treated with acid is pumped into a still containing a solution of caustic soda amounting to from 2 to 4 per cent. of the oil, and is redistilled from the soda, by which process free acid and sulphonates are more perfectly removed and the oil is improved in colour. The treatment with sulphuric acid removes tarry matters, as well as some of the more easily acted on hydrocarbons,[1] and the soda neutralizes the remaining traces of sulphuric acid as well as organic acids contained in the oil or resulting from treatment. The chemical changes which take place are by no means fully understood. Secondary reactions occur, certain of the hydrocarbons being very liable to undergo oxidation with formation of acid products, especially during the alkaline treatment. Great care and attention are, therefore, needed to produce the most highly refined oil, which is clear and bright, contains neither acid nor alkali, and does not become turbid on standing.

(*d*) **Russian Oils**.—The manufacture of lubricating oils from ostatki was commenced by V. I. Ragosine in 1876, and two years later the Russian oils were first introduced into England.[2] Up to that time naphtha and illuminating oil were the only products manufactured from the crude Caucasian petroleum, and the ostatki was either burned as fuel or entirely wasted. Even now the greater proportion is used as fuel, and only a comparatively small proportion, about 10 per cent. according to Redwood, is manufactured into lubricating oils; but, considering the enormous quantity of ostatki produced, even this small proportion amounts to a considerable volume.

The ostatki,[3] which is stored in large tanks sunk in the ground,[4] is

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[1] It is said that some valuable lubricating hydrocarbons are withdrawn by the action of sulphuric acid.

[2] *Jour. Soc. Chem. Ind.*, 1887, p. 631.

[3] See *Jour. Soc. Chem. Ind.*, 1885, p. 111 ; and 1886, p. 382.

[4] Redwood states that Messrs. Nobel have a cylindrical tank of this description holding eleven million gallons.

first pumped into raised tanks in which it is heated by steam coils to facilitate the settling of water and other impurities likely to caus frothing and explosive ebullition. The clarified oil flows by gravita tion into the stills, which are horizontal wrought-iron vessels o circular or elliptical section, waste oil being the fuel used for heat ing them. When the temperature has risen to 130° or 140° C (266°–284° F.) a fairly regular ebullition sets in, and distillatio commences at about 150°–160° C. (302°–320° F.). Superheated steam is then admitted through perforated pipes placed very near th bottom of the retort, and the distillate is collected in separat fractions as the temperature rises, until the oil coming over ha a density of 0·915 to 0·920, when the fire is extinguished. Th injection of steam is, however, continued until oil ceases to com over. The still is then left to cool, and the residue, called *goudron* o *deggut*, is run off while still hot into tanks placed outside the building The fractions collected by this process present the characteristic given in Table XVIII.

' *Solar Oil* ' is too fluid for lubrication, and is used either as heavy illuminating oil or for making oil-gas. ' *Mixing Oils* ' ar also prepared from solar oil, the chief use of which is for purpose of adulteration (*Redwood*).

' *Goudron* ' when cold is almost solid. It is used as fuel an for other purposes. Sometimes a lubricating grease is made fron it, of the nature of vaseline, by mixing it with about one-third sola oil and very gradually heating the mixture in a still to 180°–200° C Distillation' is then started by passing in superheated steam. A first a fluid oil comes over, but soon the distillate begins to partiall solidify on cooling, the proportion of solid gradually increasing unti the whole solidifies. This distillate is collected separately, unti about three-fourths of the contents of the still have come over.

TABLE XVIII.—FRACTIONAL DISTILLATES FROM
RUSSIAN RESIDUUM.

Fraction.	Description.	Distilling at °C.	Per Cent.	Specific Gravity.	Colour.
1st	*Solar Oil,*	150–170	10–12	·840–·860	Pale yellow.
2nd	*Light Spindle Oil,*	170–200	12–15	·870–·880	Yellow.
3rd	*Heavy Spindle or Light Machine Oil,*	200–250	8–10	·895–·900	Yellow.
4th	*Engine Oil,*	250–300	30–33	·908–·912	Reddish-yellow.
5th	*Cylinder Oil,*	300–320	10–12	·915–·920	Red.
Residue	*Goudron,*	...	12–15	·950	Brown black.

All the *lubricating oil distillates* have a dark colour and a strong odour. Paler coloured, odourless oils are produced from them by chemical treatment followed by redistillation, as in the case of the American oils, but as the Russian oils contain no paraffin wax the refrigerating process is, of course, omitted.

The various forms of plant used for the distillation of lubricating oils from petroleum and shale, though differing in detail, merely represent different methods of carrying out the general principles referred to on pp. 94-96, and the yield and characters of the separate fractions obtained in different factories vary according to the nature of the raw material and the demands which the manufacturer has to meet.

(e) **Shale Oils.**--Crude shale oil yields on distillation the same products as crude petroleum, viz. : —naphtha, illuminating oil, gas oil, lubricating oil, and paraffin wax. The methods of separating these products and obtaining them in a pure state are the same in principle, viz. :—fractional distillation, followed by chemical treatment of the distillates ; but the process is more complicated. Shale oil is subjected to a large number of separate distillations and treatments in order to facilitate the separation of the paraffin wax, of which the crude oil yields about 12 per cent., whilst American petroleum yields only about 2 per cent., and Caucasian petroleum none. The lubricating oils from shale are of low viscosity (spindle oils), and are all *distilled oils*, there being no products corresponding to the natural and reduced oils prepared from American petroleum.

For further information regarding the manufacture of mineral lubricating oils, drawings of the plant, etc., the reader is referred to the standard treatise on the subject by Redwood.

III. Properties and Composition of Mineral Lubricating Oils.

Mineral lubricating oils are classed commercially as 'pale' and 'dark.' The pale oils are more or less transparent, and present a variety of shades of yellow and red. The dark oils are opaque, and are either greenish- or brownish-black. Most mineral oils, unless they have been 'debloomed' by chemical treatment, are (in distinction to animal and vegetable oils) fluorescent. The smell and taste, although usually slight, are also characteristic.

The specific gravity usually ranges from about 0·860 to 0·940, though oils of higher sp. gr. are occasionally met with. The boiling-point is high, usually above 600° F. (315·5° C.) in the case of refined distilled oils. The flashing point ranges, with few exceptions, from 300° to 600° F. The cold-test or setting point varies, and depends partly upon the proportion of solid hydrocarbons present. Russian oils have the lowest setting-point, sometimes below 0° F. ; most American oils do not remain fluid below 25° F. ; Scotch oils set at about 32° F.

The lubricating oils obtained from petroleum present a much

greater range of viscosity than the fixed oils. The thinnest are more fluid than sperm oil ; the thickest are more viscous than castor oil. Scotch shale oils are only met with among the oils of low viscosity. Reference to the tables on pp. 162–166 will show how slight is the connection between specific gravity and viscosity. Among oils of a given specific gravity, natural and reduced oils are more viscous than refined oils ; and among the latter Russian oils, at low and moderate temperatures, are more viscous than American. Mineral oils lose viscosity with rise of temperature more rapidly than the fixed oils; but if the curves of absolute viscosity on pp. 168 and 169 be studied, it will be seen that this difference becomes much less marked at temperatures above 100° F. (or 150° F. in the case of cylinder oils). The loss of viscosity is greater the more viscous the oil ; and the higher the temperature above the normal, the more nearly do all oils approximate to one another in viscosity. It is not entirely owing to the greater influence of temperature on the viscosity of mineral oils that they are less perfect lubricants than the fixed oils, but partly owing to the fact that they are deficient in the property of 'oiliness,' the nature and cause of which are somewhat obscure.

Although the chemical composition of petroleum has been the subject of an immense amount of research, attention has chiefly been directed to the naphtha and illuminating oil fractions, whilst those of higher boiling-point, from which lubricating oils are prepared, have been comparatively little studied. Allen states that the lubricating oils obtained from American petroleum and from shale consist largely of olefines; paraffins are present in considerably larger proportion in the petroleum product than in the shale product, and the latter also contains small amounts of polymerized acetylenes, and possibly also terpenes. Zaloziecki has confirmed the presence of terpenes in the higher fractions from petroleum.[1] Aisinmann[2] states that the American lubricating oils consist chiefly of paraffins, and that those from Baku are composed mainly of naphthenes and olefines. More recently, Engler and Jezioranski[3] have come to the conclusion that these differences do not exist. By making analyses of petroleums from different sources, and also of the various fractions obtained by their distillation, they have found that the ratio of carbon to hydrogen increases with the boiling-point, and that in all cases the highest fractions contain, in considerable quantity, hydrocarbons which are poorer in hydrogen than those of the ethylene series. From these analyses, and from a comparison of the amount of each fraction absorbed by sulphuric acid, they conclude that the fractions boiling above 200° C., of American as well as of Russian and Galician oils, consist mainly of unsaturated hydrocarbons. Kraemer and Spilker[4] have prepared synthetical hydrocarbons, resembling in their

[1] Jour. Chem. Soc., 1894, Abs., i. 611.
[2] Jour. Soc. Chem. Ind., 1895, p. 283.
[3] Jour. Chem. Soc., 1896, Abs., i. p. 1.
[4] Jour. Chem. Soc., 1891, Abs., p. 1462.

physical and chemical characters mineral lubricating oils, by the condensation of methylbenzenes with cinnamene or with allyl alcohol in the presence of sulphuric acid. The product formed from pseudocumene and allyl alcohol had the composition $C_{21}H_{28}$, and was probably dimethyldicumylmethane ; it boiled above 300° C, and in the viscometer gave, at 15° C., the value 775 (water $= 1$), whilst the best Russian lubricating oil gave, in the same apparatus, the value 40. Kraemer and Spilker regard these bodies as the 'viscosity carriers' of mineral lubricating oils, and have proved that their viscosity increases rapidly with the number of methyl groups in the molecule. Mills states that the normal paraffins are not lubricants, and that the lubricating properties belong to one or more series of isoparaffins.[1]

Besides the fluid hydrocarbons, American and Scotch oils contain solid hydrocarbons (paraffin), and in the dark 'reduced' oils variable quantities of asphaltic and tarry bodies exist.

Mineral lubricating oils are unsaponifiable, which enables them to be easily separated from the fixed oils. In Hübl's process they absorb from 7 to 23 per cent. of iodine, according to their origin. Owing to the almost entire absence of any tendency to oxidize or develop acid, they do not as a rule gum or corrode bearings, and, if carefully refined, so as to be free from volatile hydrocarbons, they undergo but little change by use. Therefore, pure mineral lubricating oils, if occasionally filtered to remove suspended impurities, can be used over and over again, which is not the case with any of the fixed oils. Mineral oils, owing to their non-oxidizable character, are also incapable of igniting spontaneously, and when mixed in sufficient proportion with animal and vegetable oils, they reduce the risk of fire.

B.—FIXED OILS AND FATS.

Sources, Composition, and General Properties.

'Fixed' oils, so called because they are not volatile without decomposition, are found ready formed in certain tissues of animals and plants. They differ from the mineral oils in containing oxygen as an essential constituent, the proportion ranging from 9·4 to 12·5 per cent. The distinction between fixed oils and fats is only a matter of temperature. All fixed oils become fats at low temperatures, and all fats become oils at 150° F.

The fat of terrestrial animals is found in the cells of the adipose tissue, and in the case of marine animals in the blubber, from which it is melted out or 'rendered' by simple heat, or by boiling with water. The oils of plants occur mostly in the seeds or fruit, and are obtained either by expression, or by means of solvents such as petroleum ether ; oils so obtained are frequently subjected to a process of refining, in order to remove the albuminous and

[1] *Destructive Distillation*, fourth edition, p. 84.

mucilaginous matter which is expressed or dissolved out with the oil. Each of the different oil-yielding plants and animals furnishes its own peculiar oil ; hence a considerable variety of fixed oils and fats exists.

Animal oils are usually either colourless or yellow ; vegetable oils are of various shades of yellow and green, the green colour being due to the presence of *chlorophyll*, which is characteristic of this class of oils. Each kind of oil has usually a distinctive odour by which it can be identified. Fixed oils very rarely present a fluorescent appearance, unless adulterated with mineral oil.

In specific gravity they range from about 0·879 to 0·968 at 60° F. Sperm oil is the least viscous, castor oil the most, but each kind of oil has its own peculiar viscosity, which varies but little. They cannot be distilled without decomposition, the so-called 'boiling' of fixed oils being due to the escape of gases produced by destructive distillation. The solidifying points of fixed oils, and the melting-points of fats, vary considerably (see pp. 199 and 204).

A fundamental difference between fixed oils and mineral oils exists in their behaviour towards atmospheric oxygen. Mineral oils are almost indifferent to oxygen, but all the fixed oils combine with it,[1] and most of them undergo, as a result of the oxidation, changes which convert them sooner or later into solid elastic varnishes. The oils which behave in this manner are called 'drying oils,' and a few which oxidize and dry most rapidly (notably linseed oil) are used as vehicles for paint. Lubricants are selected from the 'non-drying' or less strongly drying oils, the chief of which are olive, rape, and castor among vegetable oils, and tallow, lard, neatsfoot, and sperm among animal oils.

All fixed oils are composed of fatty esters, formed by the union of alcohol radicles with fatty acid radicles. The alcohol radicle occurring in the vegetable oils and in most of the animal oils is the trivalent radicle *glyceryl*, C_3H_5, the radicle of glycerol or glycerin $(C_3H_5(OH)_3)$, and its esters, known as *glycerides*, may be represented by the formula $C_3H_5R_3$, in which R represents the fatty acid radicle. Usually several esters occur together. Those most frequently met with are triglyceryl stearate or tristearin $C_3H_5(O.C_{18}H_{35}O)_3$, triglyceryl palmitate or tripalmitin $C_3H_5(O.C_{16}H_{31}O)_3$, and triglyceryl oleate or triolein $C_3H_5(O.C_{18}H_{33}O)_3$. Stearin and palmitin predominate in the solid fats, olein in the fluid oils. Olein is the chief constituent of many of the best known lubricants, such as lard, tallow, neatsfoot, and olive oils. Until recently, natural oils and fats were believed to be mixtures, exclusively, of simple triglycerides such as the above, in which all the acid radicles contained in the molecule are alike ; but recent researches have proved that mixed triglycerides also occur, such as steáro-dipalmitin, palmito-distearin, oleo-palmito-stearin, etc.

Allied to the fats are the *waxes*, which are esters of mono- and

[1] In consequence of this property, cotton waste and similar fibrous material when saturated with many of the fixed oils, especially those of the drying class, are liable to heat and undergo spontaneous ignition (see p. 278).

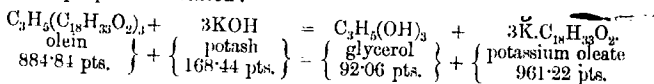di-hydric alcohols. Thus, cetyl palmitate or cetin, $C_{16}H_{33}.O.C_{16}H_{31}O$, derived from cetyl alcohol ($C_{16}H_{84}O$), is the chief constituent of spermaceti, and myricyl palmitate or myricin, $C_{30}H_{61}.O.C_{16}H_{31}O$, from myricyl alcohol ($C_{30}H_{62}O$), is the chief ingredient of beeswax. Sperm and bottlenose oils belong to this group, and are therefore known as liquid waxes, since the esters composing them are not glycerides, but are derived from mono-hydric alcohols.

· All fatty esters, by hydrolysis, are split up into alcohols and fatty acids. The change can be effected in several ways: by heating with water under pressure, by heating with sulphuric acid, or by heating with alkalis; but however produced it is known as '*saponification.*' In saponification by heating with water under pressure, both the alcohol and the fatty acid are liberated in the free state. Thus, in the case of olein, the complete change is represented by the follow-ing equation :—

$$C_3H_5(C_{17}H_{33}O_2)_3 + 3H_2O = C_3H_5(OH)_3 + 3C_{18}H_{34}O_2.$$
$$\text{olein} \qquad + \text{water} = \text{glycerol} + \text{oleic acid}.$$
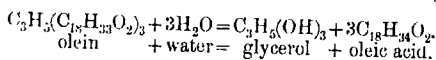
This change takes place in steam cylinders when fatty oils are used as lubricants, with the result that the fatty acids set free corrode the metal and form metallic soaps which choke the steam passages.

When saponification is effected by means of an alkali, such as potash or soda, the alcohol alone is set free; the fatty acid combines with the alkali or base, forming a *soap*. Thus, when olein is heated with a solution of potash the following change takes place, in the definite proportions stated :—

$$C_3H_5(C_{18}H_{33}O_2)_3 + \quad 3KOH \quad = C_3H_5(OH)_3 + 3K.C_{18}H_{33}O_2.$$
$$\begin{array}{ccccc} \text{olein} & & \{ \text{ potash} \} & \{ \text{glycerol} \} & \{ \text{potassium oleate} \} \\ \text{884·84 pts.} & \} + \{ \text{168·44 pts.} \} & = \{ \text{92·06 pts.} \} & + \{ \text{961·22 pts.} \} \end{array}$$

This reaction enables us to at once distinguish between a mineral oil and a fixed oil, and to separate the mineral oil from a mixture of the two. For, on boiling with potash, the hydrocarbons composing the mineral oil undergo no change, but the esters composing the fatty oil undergo saponification, forming soaps and glycerol, both of which can be washed away by water, leaving the mineral oil in the free state.

In the case of a wax like sperm oil or wool fat a complication arises, since the wax alcohols are not soluble in water, and, therefore, contaminate the mineral oil. The mixture can, however, be analysed by the method described on p. 245.

Soaps are easily decomposed by mineral acids, and the fatty acids are set free. Thus, in the case of potassium oleate and hydrochloric acid :—

$$K.C_{18}H_{33}O_2 + \quad HCl \quad = \quad KCl \quad + C_{18}H_{34}O_2.$$
$$\text{potassium oleate} + \text{hydrochloric acid} = \text{potassium chloride} + \text{oleic acid}.$$
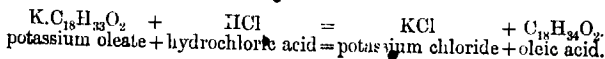
Most fatty acids, when melted, are oily liquids, which float as an insoluble oily layer on the surface of water; but a few, such as the

valéric acid of porpoise jaw oil, are soluble in water, and evaporate with the steam when the water is boiled. The fatty acids obtained by saponifying the natural oils are almost invariably mixtures, and by examining the mixed fatty acids it is frequently possible to determine the nature of the fatty oil from which they have been derived.

The chief fatty acids which are known to occur in lubricating oils are given in Table XIX.

TABLE XIX.—FATTY ACIDS OCCURRING IN LUBRICATING OILS

Series.	Name of Acid.	Formula.	Occurs chiefly in
Acetic, $C_nH_{2n}O_2$	Isovaleric	$C_5H_{10}O_2$	Porpoise jaw oil.
	Caproic	$C_6H_{12}O_2$	
	Caprylic	$C_8H_{16}O_2$	
	Capric	$C_{10}H_{20}O_2$	Coconut oil.
	Lauric	$C_{12}H_{24}O_2$	
	Myristic	$C_{14}H_{28}O_2$	
	Palmitic	$C_{16}H_{32}O_2$	Palm oil; also tallow, olive oil, and coconut oil.
	Stearic	$C_{18}H_{36}O_2$	Tallow; also palm, castor, and rape oils.
	Arachidic	$C_{20}H_{40}O_2$	Earthnut, rape, and mustard oils.
	Lignoceric	$C_{24}H_{48}O_2$	
Oleic, $C_nH_{2n-2}O_2$	Oleic	$C_{18}H_{34}O_2$	Olive oil and the animal oleins.
	Rapic	$C_{18}H_{34}O_2$	Rape oil.
	Erucic	$C_{22}H_{42}O_2$	
Linolic, $C_nH_{2n-4}O_2$	Linolic	$C_{18}H_{32}O_2$	The drying oils; also in olive and palm oils
Ricinoleic, $C_nH_{2n-2}O_3$	Ricinoleic	$C_{18}H_{34}O_3$	Castor oil.
	Isoricinoleic	$C_{18}H_{34}O_3$	
$C_nH_{2n}O_4$	Dihydroxy-stearic	$C_{18}H_{36}O_4$	Castor oil.

The *vegetable oils* chiefly used for lubrication are rape olive, and castor. Rape and olive oils are employed both alone and mixed with mineral oils. Castor oil is largely used for railway work in India, mixed with heavy mineral oil, of which it can take up a certain proportion only, the amount varying with the temperature. To produce with castor oil and mineral oil a mixture that will not, even at low temperatures, separate on standing, an equal volume of tallow oil or

lard oil must first be mixed with the castor oil. Coconut oil is said to be used in India on light-running machinery, and in this country for the preparation of mixed spindle and loom oils, but the commercial oil seems quite unsuitable for such purposes, owing to the large amount of free fatty acid which it frequently contains (see p. 116). Maize oil (corn oil) has been described as a non-drying oil and a good lubricant, but it dries as readily as cottonseed oil.[1] Palm oil is sometimes used in making the yellow grease employed for the lubrication of railway wagon axles. Hazel-nut oil and ben oil are used for the lubrication of watches and delicate mechanism.

The *animal oils* chiefly employed for lubrication are tallow, tallow oil, lard oil, neatsfoot oil, sperm oil, and porpoise jaw oil. Tallow is used for grease making, and the three following oils are chiefly employed for mixing with mineral oils. Sperm oil is used, both mixed and unmixed with mineral oil, for light machinery and spindles. Porpoise jaw oil is used for the lubrication of watches and delicate mechanism, for which a thoroughly non-drying and fairly limpid oil is required.

Rape (Colza) Oil.—Commercial rape or colza oil is obtained from the seeds of several cultivated varieties of *Brassica Campestris*, Linn., the navew or wild turnip, a plant belonging to the natural order *Cruciferae*, cultivated very extensively in France, Germany, Austria-Hungary, Roumania, and Southern Russia ; also in India and China. The principal source of European rape oil (German, rapsöl) is rape seed or cole seed, from *B. Campestris* var. *Napus*. *B. Campestris* proper, cultivated in France and Belgium under the name 'colza,' yields colza oil (German, kohlsaatol), and *B. Campestris* var. *Rapa* (*B. Rapa oleifera*, Linn.), grown in South Germany, yields the oil known as 'rubsen' (German, rubol or rubsenol). These three oils, colza, rape, and rubsen, though botanically quite distinct, are similar in their chief physical and chemical characters, and are not distinguished commercially, being all sold as rape oil.

The rape seed which is so largely imported into Europe from India for the manufacture of rape oil is the product of chiefly *B. Campestris* var. *Glauca*. Indian rape seed varies very much in size and appearance, according to the district in which it has been grown, the finest commercial varieties being known as yellow Guzerat and yellow Cawnpore, less esteemed kinds as Madras, brown Calcutta, brown Cawnpore, Ferozepore. etc. A seed known as Jamba rape,[2] which is said to yield a good oil, is occasionally exported from Kurrachi. Indian rape has some of the characters of mustard (possibly owing to the common practice of sowing the seeds together), in consequence of which the cake cannot be safely used for feeding cattle.[3] The resemblance between some kinds of Indian rape seed and white mustard seed has led to frequent mistakes and even lawsuits. Thus

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[1] *Jour. Soc. Chem. Ind.*, xviii. (1899), p. 346.
[2] For its characters see Lewkowitsch, *Analysis of Oils*, third edition, p. 578.
[3] *Kew Bulletin*, 1894, p. 96.

the seed known as 'Guzerat' resembles a mixture of ordinary rape with white mustard. The careful examination of Dr. Wittmack, of the Berlin Agricultural Museum, however, has shown conclusively that the structural characters of the seeds are those of rape and not of white mustard, and there is reason to suppose that the white as well as the dark seeds are all the produce of the same plant.[1] Watts[2] mentions two other varieties of Indian rape, viz. :—*B. Campestris* var. *Dichotoma* and *B. Campestris* var. *Toria* ; the oil from the former he terms Indian colza, and says it is chiefly used for anointing the body, that from the latter is probably mixed with the oil from the var. *Glauca.* The following results may be of interest as showing the characters of Indian rape oil extracted from the seed by ether in the laboratory :—

TABLE XX.

Physical and Chemical Characters.	Yellow Guzerat.	Brown Calcutta.	Madras.
Sp. gr. at 60° F., . . .	0·9133	0·9146	0·9140
Saponification value, per cent.,	17·50	17·42	17·45
Iodine value, per cent., . .	97·8	102·7	99·6
Oxidation test (see p. 265), .	1 grm. of the oil did not dry or become unduly thickened in 16 hours at 212° F.		

A more complete investigation of the constants of Indian rape oils expressed from different varieties of pure seeds has been published by Crossley and Le Sueur, *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 989.

Rape seed, from *B. Campestris* var. *Chinensis* (Chinese Cabbage), is cultivated extensively in China, and another variety, *B. Campestris* var. *Cernua*, in Japan. The oil of the hedge or wild radish, *Raphanus Raphanistrum*, sometimes called hedge mustard, is said to be mixed with and even substituted for rape oil in Hungary.

Rape oil is obtained from the seed either by expression or by extraction with solvents. In either case the seed is first thoroughly crushed in roller mills. In the process of expression the crushed seed is first subjected to very moderate pressure in the cold, by which a considerable quantity of oil is obtained ; the cakes are again passed through the mill, and the meal is then heated and damped in a jacketed steam-pan called a 'kettle,' which process, by rendering the remaining oil more fluid, facilitates its expression, and at the same time coagulates some of the albuminous matter of the seed and prevents it from being expressed with the oil. The heated seed-meal is then rapidly moulded into cakes and subjected to hydraulic pres-

[1] *Kew Bulletin*, 1877, p. 34 ; and 1894, p. 96.
[2] *Dict. of the Economic Products of India*, vol. i. pp 522-528

sure. In the process of extraction with a solvent, by which means the larger proportion of the rape oil of commerce is now obtained, the crushed dry seed is placed in the extraction apparatus and exhausted with petroleum spirit or carbon disulphide, and the oil is obtained by distilling off the solvent.[1]

Crude rape oil is dark in colour, and contains albuminous impurities which cause turbidity and set up fermentation, resulting in the partial decomposition of the glycerides with liberation of free fatty acids. In order to remove these impurities, it is usual to refine the oil by agitating it, whilst warm, with a strictly limited proportion (0·5 to 1·5 per cent.) of sulphuric acid (Thénard's process) sufficient to attack and char the impurities, which are more easily acted upon than the glycerides, without causing serious hydrolysis of the latter. After thoroughly agitating the oil with the acid for about ¾ to 1 hour, sometimes longer, according to the quantity and quality of the oil treated, the mixture is allowed to rest, and the suspended acid and impurities gradually settle out as a dark coloured magma ('foots'), leaving the oil bright and clear. The latter is then drawn off, washed by agitation with steam and hot water, again racked off and boiled with water a second time, allowed to settle, and 'baled' until bright.

The following results are of interest as showing the effect of the acid refining process upon the acidity and other characters of rape oil. For the samples the authors are indebted to Mr. John F. Hutcheson of Glasgow, who kindly obtained them specially from Stettin.

TABLE XXI. —EFFECT OF REFINING RAPE OIL BY THÉNARD'S METHOD.

Physical and Chemical Characters.	Brown Rape Oil from freshly crushed seed.	Brown Rape Oil clarified by settling.	Refined Rape Oil.
Free (oleic) acid, per cent.,	1·58	0·98	2·26
Specific gravity at 60° F.,	0·9146	0·9147	0·9141
Relative efflux time at 60° F.,	104	101	100
Saponification value, per cent.,	17·42	17·36	17·30
Iodine value, per cent.,	101·8	100·9	102·3
Maumené thermal value, ° C.,	57·0	56·25	56·75
Unsaponifiable matter, per cent.	0·98	0·95	0·75

Rape oil refined by Thénard's process is apt to contain traces of free sulphuric acid (see p. 313).

As the tendency of the acid refining process is to increase the acidity of the oil, an alkaline process would appear preferable. Everard's process, which consists in agitating the oil with a weak

[1] For a detailed description of oil mill plant, see *A Practical Treatise on Animal and Vegetable Fats and Oils*, by W. T. Brannt, vol. I. chaps. x. and xi.

solution of caustic soda, has been applied to rape oil. One difficulty in the practical working of such processes is the tendency of the oil and alkaline liquor to form emulsions which are troublesome to separate, and to avoid this it has been proposed to use a liquid formed by melting soda crystals in their water of crystallization (*Hageman*), which is said not to emulsify. Milk of lime and calcined magnesia have also been suggested.

Rape oil has been found to contain the glycerides of rapic and erucic acids, but the high iodine value of the oil points to the presence also of an acid or acids of the linolic or linolenic series. Glycerides of saturated fatty acids occur in very small proportion in rape oil and include arachidic and, probably, lignoceric acids. Ponzio[1] found 0·4 per cent. of arachidic acid in one sample. Alén[2] found arachidic acid in the oil from Guzerat seed, but not in that from the European varieties. Archbutt[3] found 1·43 per cent. of arachidic (and lignoceric) acids in rape oil extracted by means of ether from Guzerat seed, and 1·14 per cent. in commercial (Stettin) rape oil expressed from rape and rubsen seed. Of 51 samples of commercial rape oil which were specially examined by Renard's process, about two-thirds were found to contain arachidic acid. Indian rape oil from *B. glauca* seems to contain more of this acid than the European oil, and the extracted oil more than the expressed oil ; of the latter, the cold-pressed oil probably contains less than the hot-pressed. Arachidic and lignoceric acids are also contained in mustard oil.

Rape oil is by no means a non-drying oil, and as different samples vary considerably in oxidizing property, it is necessary to make a careful selection of the oil intended for lubricating. Rape oil is not suitable for delicate machinery.

According to Schaedler, rape oil sets or solidifies at $-2°$ to $-10°$ C. ; but Holde states that all rape oils sooner or later solidify at $0°$ C. ($32°$ F.). The following experiment was made by one of the authors. Some genuine refined rape oil was placed in a glass tube, immersed in melting ice for three hours without stirring, and then for three hours longer, stirring at intervals. It remained clear and fluid. Some of the same oil, previously frozen, having been added, the oil was kept in ice for three hours longer, with occasional stirring, but the frozen oil slowly melted. The temperature was then gradually reduced to $14° - 16°$ F. ($-10°$ to $-9°$ C.), and the oil became very turbid, but after remaining for two hours at this temperature, with stirring, it did not lose its fluidity. After still further reducing the temperature to $11°$ F. ($-11·6°$ C.), and stirring, the oil solidified in about half an hour.

Black Sea Rape Oil. Ravison Oil.—Oil expressed from the seed of the Black Sea district, known as ravison oil, is inferior in quality

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[1] *J. für pr. Chem.*, xlviii. (1893), p. 487.
[2] *Svensk. Kemisk Tidskrift*, 1893, p. 179.
[3] *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 1009.

to, and cheaper than, ordinary rape oil ; it has a higher sp. gr., higher saponification and iodine values, and more strongly drying properties than ordinary rape oil, and is usually of inferior quality for lubricating. The unacknowledged admixture of this oil with rape oil must therefore be regarded as adulteration. The chief properties of the oil are shown by the results in Table XXII. The samples of Black Sea oil and seed were kindly supplied by Messrs. Seaton & Co., of Hull.

TABLE XXII.—PROPERTIES OF BLACK SEA RAPE OIL.

Physical and Chemical Data.	Kustendje Rape Oil made from Wild Rape Seed from the Black Sea Extracted by the CS_2 process.	Black Sea Rape Oil Expressed and Refined. Two Samples.		Oil extracted in the Laboratory from Black Sea Rape Seed Two Samples.		Oil extracted from Seed (b) after picking out 13·3 % of Foreign Seeds.
		(a)	(b)	(a)	(b)	
Free acid, as oleic acid, %	2·43	6·02	2·8	..	..	.
Sp. gr. at 60° F ,	0·9183	0·9200	0·9217	0·9211	0·9200	0·9200
Viscosity at 60° F ,	About 6 lower than that of re-fined Stettin rape oil.	About 13 % lower than that of refined Stettin oil.				
Saponification value,	17·79	17·93	17·80	17 93	17·81	17·81
Iodine value, .	110·2	110·7	121·7	111·5	108·9	109·3
Maumené thermal value, ° C.,	65·8	76	..			..
Unsaponifiable matter, %	1·45	1·66	1·64	..	.	..
Arachidic acids obtained by Renard's process,	0·79 (m.p. 70·4° C.)	..	.			..
Colour Reactions.						
Millian test, .	neg	neg.	neg	..		.
Badouin's test,	..	.	neg	..	..	.
Oxidation test. (1 grm. of oil exposed on a watch glass at 212° F. for 16 hours),	Rather more dried than Stettin oil, but not more thickened.	Badly dried and much more thickened than Stettin oil.	..	Dried and much thickened.		
Properties of Mixed Fatty Acids.						
Sp. gr. at $\frac{212°}{212°}$ F., .	..	..	0·8802		"	
Iodine value, .	..	..	126·1			.

For the constants of genuine rape oil, and the detection of adulteration,

Olive Oil.—Olive oil is obtained from the fruit of the cultivated olive tree, *Olea Europœa Sativa*, the numerous varieties of which are grown chiefly in the countries bordering the Mediterranean, also in California and other countries where the climate is suitable. The fruit is very rich in oil, which is contained chiefly in the fleshy mesocarp, but also in the kernel and shell (endocarp).

The finest olive oil is obtained[1] by hand picking the olives before they become too ripe, gently pressing them by hand in cloths, and collecting the oil which exudes. The limited quantity of '*virgin oil*' thus obtained appears to be used as salad oil, and some of it as a lubricant by watchmakers; it is purified by agitation with water, allowing the mucilaginous matter to subside, and skimming off the clear oil from the surface. Oil nearly as fine is obtained on the large scale by crushing the ripe olives under millstones or between iron rolls, usually, though not always, without breaking up the kernels, and pressing the pulp, without heating it, in bags or mats of esparto grass under very moderate pressure. After purifying by agitation with water and settling, this cold-pressed oil is called '*superfine oil*,' or frequently '*virgin oil*,' and is used chiefly as a salad oil. The once-pressed marc is broken up by bending the mats back and forth by hand, moistened with hot water, and again pressed, more strongly than before, yielding '*ordinary oil*,' or 'oil of the second pressing,' which is said to be but slightly inferior to the virgin oil. The twice-pressed marc, after being stored for a time and allowed to ferment (which facilitates the extraction of ~~the oil~~, is reground so as to crush the olive stones, and after being stirred up with boiling water, is subjected to the heaviest pressure obtainable with the appliances used; oil of inferior quality, called '*pyrene oil*' or '*bagasse oil*,' is thus obtained. The residual marc still contains some oil, which is extracted by means of carbon disulphide or petroleum spirit, and is known as '*sulphocarbon oil*.' The last two kinds of oil are dark green or brown in colour (due to the presence of chlorophyll), consist largely of decomposition products, are very acid, and are fit only for soapmaking or dyeing. Some of the dark-coloured oils, even when nearly neutral, are of inferior quality for lubricating, owing to their tendency to thicken and 'gum' on the bearings. Oils known as '*huile tournante*' and '*huile d'enfer*'[2] are much decomposed and highly acid olive oils recovered from the watery residues of the oil pressing, and, though in demand for dyeing Turkey red, are quite unfit for lubricating.

In the refining of the crude olive oil, it is sometimes allowed merely to rest in large tanks until the 'mucilage' has deposited, undergoing during the time more or less decomposition, and often becoming spoiled for lubricating. Sometimes the oil is refined by washing with

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[1] See Alder Wright, *Oils, Fats, Waxes, etc.*, second edition, p. 420.

[2] '*Enfer*' is the name given to the stone or tile cistern in which the water is left for the oil to rise.

water alone, and sometimes it is washed with caustic soda. In France it is usual to filter the oil through cotton or paper.[1]

Olive-kernel Oil was formerly believed to be quite different in properties from ordinary olive oil (the oil of the mesocarp), having a sharp and bitter taste, a dark green or brown colour, and being readily soluble in alcohol, owing to the presence of much free fatty acid; but it has been shown by Klein[2] that the characteristics hitherto assigned to olive-kernel oil are really those of *pyrene* oil or *bagasses* oil, the dark coloured and more or less decomposed oil expressed from the stones and refuse of the first and second pressing of the olives. Pure olive-kernel oil, prepared both by cold and by warm expression from the kernels alone, without any admixture of the pulp, was found to have the following characters, as compared with a sample of 'bagasses' oil :—

	Olive-kernel Oil.		*'Bagasses' Oil.*
Sp. gr. at 60° F., . . .	0·9186 to	0·9191	0·928
Saponification value, per cent.,	18·23	„ 18·38	19·05
Iodine value, ...	87·0	„ 87·3	71·6
Free fatty acids, per cent., .	1·00	„ 1·78	71·12

From these results it appears that pure olive-kernel oil is somewhat higher in specific gravity and iodine value, and lower in saponification value, than ordinary olive oil, but it does not naturally contain an excess of free fatty acids. The characters of commercial olive oil must evidently depend to some extent upon whether the process of extraction has or has not been such as to include the kernel oil.

Olive oil has been stated to contain about 28 per cent. palmitin, 67 per cent. olein. and 5 per cent. linolein (*Hazura*). Later researches, however, have shown that the proportion of glycerides of solid fatty acids in different olive oils is extremely variable, and usually very much less than the above (*Tolman* and *Munson*). Stearin is absent (*Hehner* and *Mitchell*). According to Tolde, the solid fatty acids are partly present as mixed glycerides. Traces only of arachin have been found in genuine olive oil, and Klein states that in olive-kernel oil he could find none.

For the characters of genuine olive oil and the detection of adulteration, see p. 316.

Castor Oil.—Castor oil is obtained from the seeds of the castor oil plant, *Ricinus communis*, Linn., of which there are numerous varieties. The plant is indigenous to India, but is also cultivated extensively in the United States, France, Italy, Algeria, etc. It grows wild in Formosa,[3] and the oil is for the most part wasted ; but in Java the plant is cultivated, and the export of castor oil is likely to become an important industry.[4] Two varieties of the plant are

[1] A good description of the olive oil manufacture in France, by U.S. Consul-General Skinner, was published in the *Chem. Trade Journal*, xxxi. (1902), p. 5.
[2] *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 1055 ; *Analyst*, xxiii. (1898), p. 284.
[3] *Jour. Soc. Chem. Ind.*, xii. (1893), p. 769.
[4] *Ibid.*, xiv. (1895), p. 321.

recognized by Indian cultivators, one small-seeded and the other large-seeded. The oil from the former is the most highly esteemed, and is chiefly used for medicinal purposes; it is expressed from the crushed seed without the aid of heat ('cold-drawn'), and after careful refining by heating with water is straw-yellow to greenish-yellow in colour, and nearly odourless. The oil for lubricating and burning is mostly got from the large-seeded kind, and is expressed partly cold and partly hot. The crude oil is refined by boiling it with water; soluble matters (starch, gum, etc.) are dissolved, and albumen is coagulated; the oil is then clarified by filtering or settling. In India an ancient process, which still survives, consists of first roasting the seeds to coagulate albuminous matters and facilitate the extraction of the oil, subsequently crushing, boiling with water, and skimming off the oil which rises to the surface. Oil thus obtained is often very dark in colour, and odorous. It is sometimes exported in this condition, at others it is bleached by exposure to the sun, treated with charcoal, and filtered through flannel or paper.[1]

Castor oil consists mainly of triricinolein, the glyceride of two isomeric hydroxylated acids, ricinoleic and isoricinoleic ($C_{18}H_{34}O_3$). Small quantities of tristearin and of the glyceride of dihydroxystearic acid ($C_{18}H_{36}O_4$) are also present, but palmitin and olein are absent.

Castor oil, in very cold weather, is liable to deposit a solid fat, but it congeals only at very low temperatures. It does not readily dry on exposure to the air, but turns rancid by oxidation.

Owing to its peculiar composition, castor oil differs remarkably in solubility from most fixed oils. Thus, it is easily soluble in alcohol (other oils being but sparingly soluble), and it is almost insoluble in petroleum spirit and in mineral burning and lubricating oils (in which other fixed oils are easily soluble). The ready solubility of castor oil in alcohol has been made the basis of a valuable test for the presence of adulterants in this oil (see p. 319).

The limited extent to which castor oil and mineral oils are mutually soluble is of importance in the preparation of mixed lubricants containing the former. At 59° F. (15° C.) castor oil is practically insoluble in petroleum spirit and in burning oil. In '865' Scotch shale oil, at the same temperature, it dissolves to the extent of about $1-1\frac{1}{2}$ per cent.; '890' shale oil dissolves about $2-2\frac{1}{2}$ per cent. of it; and '907/12' American mineral oil dissolves rather more. Therefore, at the ordinary temperature, castor oil is very sparingly soluble in mineral oils; the solubility is greater the more dense and viscous the mineral oil; it increases with rise of temperature and diminishes as the temperature falls.[2]

On the other hand, castor oil is able to dissolve mineral spirit and mineral oils in proportions which decrease as the sp. gr. of the

[1] *Jour. Soc. Chem. Ind.*, xii. (1893), p. 770.
[2] By heating castor oil in an autoclave to 260°–300° C. under a pressure of four or six atmospheres for about ten hours, it is said to become miscible with mineral oil in any proportion. Eng. Pat. 24935 of 1905.

mineral oil increases. The following table shows the maximum
volumes which were found to give a clear solution at 59° F. (15° C.)
with 10 c.c. of pure castor oil.

TABLE XXIII.

Mineral Oil Employed.	Sp. Gr. at 60° F.	Maximum Volume miscible with 10 c.c. of pure Castor Oil at 59° F.
Mineral (petroleum) spirit, . . .	0·692	9·2 c.c.
'White Rose' petroleum, . .	0·788	5·5 c.c.
Scotch shale oil, ...	0·865	3·7 c.c.
„ „ . .	0·890	2·45 c.c.
American pale mineral oil, . . .	0·907·0·912	1·7 c.c.

Although pure castor oil almost refuses to mix with mineral
lubricating oil, the difficulty entirely disappears if a third oil such as
rape, tallow, or lard oil is present, a clear mixture of the three being
readily obtained. Pure castor oil mixes with refined rosin oil in all
proportions.

Palm Oil. – Palm oil or fat, which is used to a limited extent for
making railway wagon grease, is obtained from the fleshy covering
(mesocarp) of the fruit of the oil-palms, *Elais guineensis* and *E.
melanococca*, which flourish in West Africa. The fruit is gathered
by the natives and stored in holes in the ground until the pulp has
become softened by decomposition ; it is then pounded, and after the
kernels have been separated the pulp is heated with water until the
oil begins to exude ; it is then squeezed in rough nets, and the oil
which runs out, mixed with more or less fibre, dirt and water, is
collected, and forms the palm oil of commerce. It is no' surprising
that the fat prepared in this crude fashion is much decomposed, and
consists, always largely, often chiefly, of free fatty acid. It is on that
account a most unsuitable material for making lubricating grease.
According to de Schepper and Geitel,[1] the most neutral brands are
the following: Lagos, Loando, Old Calabar, Gold Coast, Sherboro,
and Gaboon. The percentage of neutral fat ranges from 58 ·68 per
cent. in the first-named to 79-93 per cent. in the last-named brand.

Palm oil is, at ordinary temperatures, a soft fat melting at 80°-97°
F., when fairly rich in neutral fat ; the presence of much free fatty acid
may, however, raise the melting-point to 108°-109° F. The chief
constituents are free palmitic acid, palmitin and olein, with small
quantities of linolein, stearin, and another fat. The colour varies from
yellow to deep red. The odour of the fresh fat is pleasant and quite
characteristic.

Palm Nut Oil. —Palm-kernels contain an oil or soft fat which is
quite different from palm oil. In chemical composition and char-

[1] *Dingl. Polyt. Jour.* 245, 295.

acters it closely resembles coconut oil, having an exceptionally high saponification value (24·3–25·0 per cent.) and a very low iodine value (10–17·5 per cent.). It does not appear to be used as a lubricant.

Coconut Oil.—Coconut oil is obtained from the white pulp of the common coconut, the seed of the coconut palm *Cocos nucifera*, which flourishes abundantly in the tropical Pacific islands, the West Indies, tropical America, etc. The oil is obtained either by expression from the more or less decomposed pulp (native method), or by expression and extraction with a solvent from the dried pulp ('copra') which is imported into Europe for the purpose. The chief use of the oil is for candle and soap-making, but, according to Hurst, it is used as a lubricant for light-running machinery in India, and in this country neutral coconut oleine is employed in admixture with mineral oil as a lubricant for spindles, looms and other machinery. A brief description of the oil is therefore necessary.

Commercial coconut oil is at ordinary temperatures in this country a soft white fat, melting to a limpid oil at 68°–82° F. It easily turns rancid, and usually contains a more or less considerable quantity of free fatty acids, ranging from 5 per cent. to as much as 25 per cent., according to Lewkowitsch. It does not, therefore, possess the properties of a desirable lubricant. Coconut oil has a complex and unusual composition, consisting largely of the glycerides of lauric and myristic acids, with some palmitic and olein and a notable proportion of volatile acids, caproic, caprylic, and capric ; consequently, it differs remarkably from all oils and fats except palm-nut oil, which it very closely r esembles.

Ben Oil.[1]—Ben or behen oil is expressed from the seeds or nuts of *Moringa pterygosperma and M. aptera*, trees which are natives of Egypt, Arabia, Syria, and the East Indies, and which have been cultivated for many years in tropical America. The first-pressed oil is white or pale yellow in colour, odourless, and has a sweetish flavour. By stronger pressing, a darker coloured oil is obtained, having a bitter and somewhat sharp taste. Ben oil is said not to become rancid by long exposure to the air. It is fluid at 20° C., somewhat viscid at 15° C., begins to deposit a solid fat at 7° C. and solidifies at 0° C. It contains the glycerides of stearic, palmitic, behenic and oleic acids. That portion of the oil which remains fluid at 7° C. is used for the lubrication of delicate mechanism, including watches.

Hazel-nut Oil.[1] - This oil is obtained from the seeds or nuts of *Corylus Avellana*, the common hazel. The nuts are known as filberts, cobs, Barcelona nuts, etc. They contain 50 to 60 par cent. of a golden-yellow coloured oil, which is used to some extent as a lubricant for delicate mechanism. The oil has a characteristic odour, and according to Hanus (*Zeits. f. Untersuch. Nahr. u. Genussmittel*, 1899, ii. (8), 617) it is composed of the glycerides of oleic, palmitic, and stearic acids.

Tallow.—Tallow is the fat of certain ruminant animals, separated

[1] See Schaedler, *Technologie der Fette und Oele.*

from the enveloping membrane of the tissue by the process of melting or 'rendering.' Beef tallow is obtained from oxen, mutton tallow from rams, ewes, bucks, and she-goats.

The rendering of the fat on a small scale is effected by heating the tissue, either alone or with the addition of water, in an open pan over a fire, continually stirring to prevent burning, until the membrane has shrunk together and can be strained off; preferably, the pan is heated by means of a steam-jacket, which admits of more perfect control of the temperature. On a larger scale, a more complete separation of the fat from the tissue is effected by heating the latter in strong closed digesters, into which live steam under a pressure of 50–70 lbs. per square inch is admitted, and the liberated oil which rises to the surface of the condensed water is drawn off through a cock. Another method consists in boiling the fatty tissue in open vessels with water containing sulphuric acid or caustic soda, by either of which the nitrogenous membrane of the cell walls is chemically broken down and the fat liberated. The use of sulphuric acid would be objectionable in rendering tallow intended for lubricating because it causes partial hydrolysis of the glycerides and increases the proportion of free fatty acids; but the employment of caustic soda, which neutralizes and dissolves the fatty acids, would be advantageous. In rendering tallow for lubrication, the main points to be attended to are to use only fresh fat, which has not had time to undergo decomposition, and to remove, by settling and straining all water and fragments of membrane which, by subsequent decomposition, might cause the resulting tallow to develop acidity.

Neutral tallow was, until recently, believed to consist almost exclusively of the simple glycerides stearin, palmitin, and olein, and to be softer in proportion to the amount of olein contained in it. The presence of several mixed glycerides has, however, now been proved and traces of linolic and linolenic acids are said to have been detected The relative proportions of stearin, palmitin, and olein in tallow vary according to the nature of the animal, its sex, breed, age, food and the part of the body from which the fat is taken. The fat from the male is usually harder than that from the female, and mutton tallow is, as a rule, harder than beef tallow; but, taking the average the proportion of olein in tallow is about 46 per cent., and the remainder consists chiefly of stearin and palmitin in about equal proportions.

Of the various descriptions of tallow (Russian, North American beef, South American beef, Australian beef, Australian mutton home refined, etc.), average South American beef is usually the least acid (see p. 212) and, therefore, the best adapted for lubrication and for general application to metal; but there is no reason why preference should be given to any particular brand, if the results of chemical and physical tests prove the tallow to be genuine and of good quality.

Tallow Oil.—Tallow at the ordinary temperature of, say, 60°–80

F, is a mechanical mixture of solid and fluid fats, in which the former predominate to a sufficient extent to give the appearance of solidity to the whole. If subjected to pressure, the fluid portion can be squeezed out, and is known as *'tallow oil'* or *'tallow oleine'*; the solid press-cake forms *'tallow stearine,'* and is used in the candle manufacture. The separation is facilitated by allowing the melted tallow to cool very slowly, without disturbance, in large tubs at a temperature of 70°–80° F.; the crystallization of the solid portion then takes place in small granular particles resembling seeds, whence the process is known technically as 'seeding.' Some of the fluid portion drains through coarse flannel cloth placed upon perforated diaphragms near the bottoms of the tubs, the remainder is obtained by subjecting the semi-solid residue to pressure in canvas bags, as in the manufacture of lard oil (*q.r.*).

Tallow oil differs, therefore, from tallow chiefly in the proportion of olein which it contains, and this proportion, and therefore the setting-point and some other characters, such as the iodine value, must vary according to the temperature at which the oil has been expressed.

Tallow oil, as a lubricant, is used chiefly for mixing with mineral oils.

Lard Oil.—Lard oil, expressed from rendered pig's fat or lard, is prepared in a similar manner to tallow oil. The more or less chilled lard is placed in close-textured woollen bags between wickerwork, and is subjected to moderate but long-continued hydraulic pressure (about 10 cwts per square inch for eighteen hours). As in the case of tallow oil, the solidifying-point and other characters of the oil depend upon the temperature at which it has been expressed, winter-pressed lard oil containing less of the solid constituents of the lard than that expressed in warmer weather.

Prime lard oil is a nearly colourless, pale yellow or greenish coloured oil, highly esteemed as a lubricant, and consisting of olein with variable proportions of stearin and palmitin. The viscosity is the same as that of olive oil. The setting-point may vary from about 40° F. (4·4° C.) to several degrees below the freezing-point of water.

Neatsfoot Oil.—Neatsfoot oil is obtained by boiling the feet and hocks of oxen with water. The feet are first skinned [1] and slit longitudinally with a knife, which is passed between the sections of the hoof and continued between the long bones. A small mass of fat found near the hoof is scooped out with the knife and set apart for the preparation of the best quality of oil (see below). The hoofs are washed in cold water, and then boiled with water in open pans over a fire; the oil which rises to the surface of the water is skimmed off, and forms an inferior grade of neatsfoot oil. After about three hours' boiling, the tissues between the horny hoof and the last digit bone are sufficiently softened to allow of the latter being easily scooped out of the hoof with a knife. These 'cores,' consisting of bone,

[1] Spon's *Encyclopædia*, vol. iv. p. 1868.

gelatinous matter, and fat, together with the small mass of fat found near the hoof referred to above as being separated before boiling, are put into a separate pan of fresh water and boiled together for the extraction of the best kind of neatsfoot oil. Ten neat's feet yield from 2 to 2½ pints of a pale yellow, nearly odourless oil, which, on standing in a cold place, deposits a solid fat. The portion which remains fluid at a low temperature is used as a lubricant for clocks. Neatsfoot oil was formerly much esteemed and largely employed as a lubricant for engines and heavy machinery; it is now used, like lard and tallow oils, chiefly for mixing with mineral lubricating oils. The extensive demand for neatsfoot oil in the leather trade has probably diminished its employment as a lubricant.

Whale Oil.—Whale oil proper is obtained from the blubber of the Greenland or Arctic 'right' whale, *Balæna mystíretus*; but commercial whale oil includes the oil from the Southern right whale, *Balæna Australis*, and various other species of *Balæna* and *Balænoptera* (fin-backed whales) belonging to the tribe of *Balænoidea* or whalebone-yielding whales.

The oil which naturally exudes from the blubber of these animals, and which is also obtained by heating it with water, is mainly glyceridic in character, and may be distinguished at once from the sperm oils by its high specific gravity (above 0·919), and by yielding less than 4 per cent. of unsaponifiable matter. Whale oil even of the best quality has marked drying properties, and is not fit for use as a lubricant; it is said to be used to some extent for mixing with mineral lubricating oil.

Sperm Oil. Arctic Sperm (Bottlenose) Oil.—These oils, obtained from two different kinds (genera) of whale belonging to the family *Physeteridæ* (toothed whales possessing no functional teeth in the upper jaw) are so similar in composition and general characters that they may conveniently be described together. Tr·e sperm or 'Southern sperm' oil is obtained from the head-cavities and blubber of the Cachalot or great Sperm whale, *Physeter macrocephalus* (sub-family, *Physeterinæ*), formerly found in all seas up to 70° northern and southern latitudes, but now more scarce, and confined chiefly to the Pacific and Indian oceans. Arctic sperm or bottlenose oil is obtained from the much smaller Bottlenose whale, *Hyperöodon rostratus* (sub-family, *Rhynchoceti*), which is caught principally in the Arctic seas between Iceland and Spitzbergen. Both crude oils contain spermaceti—sperm oil much more than bottle-nose—which crystallizes out on cooling; it is separated by straining the oil through bags, and is used for the manufacture of sperm candles. Sperm oil is, therefore, liable to deposit spermaceti unless it has been bagged at a very low temperature. Allen states that practically the whole of the spermaceti is deposited by cooling the oil to 4° C. (39·2° F.).

Neither sperm nor bottlenose oils contain glycerides; they consist entirely of the esters of mono-hydric alcohols, and are, therefore,

chemically classed as fluid waxes. According to Lewkowitsch,[1] the nature both of the alcohols and of the fatty acids is at present unknown.

Sperm oil is pale yellow in colour, and when of good quality has only a faint odour. Unrefined Arctic sperm oil is usually darker in colour than Southern sperm oil, and has a more or less unpleasant odour and flavour, but the deodorized Arctic sperm oil of commerce closely resembles Southern sperm oil.

The low viscosity of the sperm oils at 60° F. distinguishes them from many other fixed oils. With rise of temperature both oils maintain their viscosity better than other fixed lubricating oils; this is shown by the following series of ratios, which have been calculated from the results in Table XXXIV. (pp. 162–165).

TABLE XXIV.—RATIOS OF VISCOSITY OF SPERM, OLIVE, AND RAPE OILS.

Oil.	60° F.	100° F.	150° F.	212° F.
	Comparative times of Efflux.			
Sperm, ...	100	46·5	25·8	18·1
Olive, ...	100	38·6	17·3	9·9
Rape, ...	100	29·4	17·6	9·8
	Comparative Viscosities.			
Sperm, ...	100	44·5	20·2	11·0
Olive, ...	100	37·4	15·3	6·9
Rape, ...	100	37·7	15·8	7·2

Porpoise Jaw Oil; Dolphin (Blackfish) Jaw Oil and 'Melon' Oil. —These very similar and remarkable oils are obtained from the soft fat of the head and jaw of two marine animals belonging to the family *Delphinidæ*, viz. :—the common porpoise, *Delphinus phocæna*, and the bottlenose dolphin, *Delphinus globiceps*. The fat is first washed in fresh water, then put into covered tins and heated for several hours in a closed digester with steam under the pressure of about ten pounds per square inch. The tins are then opened, and the liberated oil is poured off from the coagulated membrane and washed with water. It is then exposed to a low temperature, and the portion which remains fluid is separated. This oil, carefully strained to remove all solid fat, is a straw-yellow, limpid liquid. It is specially prepared in the United States for lubricating watches and other delicate mechanism, and commands a very high price. Chemically, it consists largely of the glycerides of valeric and other volatile fatty acids of the acetic series.

'**Melon Oil**' derives its name from the shape of the mass of fat

[1] *Analysis of Oils, etc.*, third edition, pp. 866–867.

taken from the head of the dolphin, reaching from the spout-hole to the end of the nose, and from the top of the head to the upper jaw. When taken off in one piece it has the shape of a half water-melon, weighs about 25 pounds, and yields about 6 quarts of oil.

Specimens of these oils, and of the crude oils from which they are obtained, have been examined by Moore,[1] with the following results:—

TABLE XXV.— PROPERTIES OF PORPOISE AND DOLPHIN JAW OILS.

	Description of Oil.	Saponi-fication Value.	Hehner Value.	Total Volatile Fatty Acids as Valeric Acid.	Reichert Value, c.c. required by 2·5 grms.	Iodine Value.
1	Porpoise jaw oil, skimmed and strained.	25·37	72·05	19·91	47·77	49·6
2	Porpoise jaw oil, skimmed and strained.	27·23	68·41	24·30	56·00	30·9
3	Dolphin jaw oil, skimmed and strained.	29·00	66·28	28·17	65·92	32·8
4	Porpoise jaw oil, un-strained.	14·39	96·50	1·64	2·08	76·8
5	Dolphin body oil.	19·73	93·07	2 71	5·60	99·5

A sample of porpoise jaw oil examined by Steinbüten had a Reichert-Meissl value of 131·6.

A small sample labelled '*Superfine Watch Oil*,' manufactured by Ezra Kelley of New Bradford, Mass., obtained from a Derby watch-maker, had a pale golden-yellow colour, a sickly odour, and gave the following results :—

Sp. gr. at 60° F.,   0·930.

Viscosity at 60° F.   { Thicker than sperm oil. Comparative runnings from a 5 c.c. pipette showed the viscosity to be about 1·3 times that of sperm oil ; =about 0·55 in absolute measure.

Reichert-Meissl value, 115·1.
Unsaponifiable matter, 10·6%. (Easily soluble in 90 per cent. alcohol, and resembling in appearance the wax alcohols of sperm oil.)

C.—'BLOWN' or THICKENED OILS.

These are fixed oils, usually rape or cottonseed, artificially thickened by a process of limited oxidation, which consists in forcing a current of air through the heated oil. The oil, contained in a tall

[1] *Jour. Amer. Chem. Soc*, xi. (1889), p. 155.

cylindrical iron vessel, is first raised to a temperature of about 170° F. by a steam-coil. Air is then blown through it in streams of bubbles, at first cautiously, to avoid too rapid a rise of temperature and frothing over of the contents of the vessel, afterwards more vigorously until the required viscosity is attained. Steam is shut off before commencing to blow air, as, by the process of oxidation, sufficient heat is evolved not only to maintain but to raise the temperature of the oil, and, in order to avoid too great a rise of temperature, provision should be made for passing, if necessary, a current of cold water through the steam-coil. Veitch Wilson states[1] that the temperature is usually allowed to rise to from 200° F. to 250° F., according to whether the quality of the product or the time occupied in the process is of the greater importance ; the time may thus vary from eighteen to forty-eight hours. Very irritating vapours, containing acetic and acrylic acids, are given off during the process, and are conveyed away by a pipe in the cover of the vessel.

Oils thus treated increase in density as well as in viscosity, and the blowing is continued until the desired specific gravity is attained. According to Veitch Wilson, the blown oils produced commercially for lubrication range in specific gravity from 0·955 to 0·985 at 60° F., and their viscosity at 180° F. ranges from that of castor oil at 60° F. to about four or five times that of castor oil. Jenkins states that blown oil of sp. gr. 0·975 at 60° F., which is largely used, has at 140° F. about double the viscosity of rape oil at 60° F., and about ten times that of rape oil at 140° F.

Blown oils have a characteristic nauseous odour. Though sparingly soluble in alcohol, they are somewhat more soluble than the untreated oils, and they readily dissolve in petroleum spirit. They do not mix with mineral lubricating oils in all proportions, a certain minimum amount (usually 20–30 per cent.) of blown oil being necessary to give a clear solution ; this minimum is greater the lower the temperature, so that a mixture which is clear when warm may separate on cooling, and it varies according to the specific gravity and origin both of the mineral oil and of the blown oil.

The nature of the chemical changes which occur during the blowing process has been studied by Fox and Baynes,[2] Thomson and Ballantyne,[3] and Lewkowitsch,[4] but is still imperfectly understood. Hydroxylated compounds are formed, the acetyl value of the oil largely increases, and the iodine value diminishes. Glycerides of insoluble fatty acids become largely converted into glycerides of soluble, chiefly non-volatile acids, and the saponification value of the oil is increased. There is an increase of 1½ to 2 per cent. in the free fatty acids, but the percentage of unsaponifiable matters is not much changed. The evolution of heat in Maumené's test is also much increased. The mixed fatty acids from blown oils are largely oxidized

[1] Carpenter and Leask, *Soap, Candles, Lubricants, etc.*, pp. 268–272.

[2] *Analyst*, xii. (1887), p. 33.   [3] *Jour. Soc. Chem. Ind.*, xi. (1892), p. 506.

[4] *Analyst*, xxiv. (1899), p. 323 ; xxvii. (1902), p. 139.

acids insoluble in petroleum ether, and are also found to contain lactones. Jenkins finds that the melting-point of the mixed fatty acids generally remains sufficiently near that of the acids from the original oil to indicate the nature of the latter. The results in Table XXVI were obtained by Thomson and Ballantyne, and those in Table XXVIA. by Lewkowitsch.

TABLE XXVI.—CHEMICAL CHANGES PRODUCED BY BLOWING.

Chemical and Physical Data.	No. 1. Pure Rape Oil.	No. 2 Partially Blown Rape Oil prepared from No. 1.	No. 3. Blown Rape Oil prepared from No. 1.	No. 4. Commercial Blown Rape Oil.	No. 5. Commercial Blown Cotton seed Oil, 'Lardine.'	No. 6. Pure Sperm Oil.	No. 7. Blown Sperm Oil prepared from No. 6.
Sp. gr. at 60° F. (15·5° C.)	0·9141	0·9275	0·9615	0·9672	0·9740	0·8799	0·8989
Free (oleic) acid,	5·10	5·01	7·06	4·93	3·48	1·97	3·27
Saponification value,	17·39	18·30	19·49	19·77	21·32	13·04	14·23
Insoluble acids (Hehner value),	94·76		85·94	82·40	84·07	.	.
Soluble non-volatile acids,	{0·52}		9·20	11·16	9·00		
Soluble volatile acids,		.	0·82	1·90	1·94		
Iodine value,	100·5	88·4	63·2	63·6	56·4	82·1	67·1
Specific temperature reaction,	135			253	227	..	..
Unsaponifiable matter,	0·65		0·76	2·80	·00	36·32	34·85
Fatty Acids.							
Iodine value of insoluble acids,	.	..	66·5	70·2	62·7		..
Molecular weight of insoluble acids,	..		327	317	296		..
Molecular weight of soluble non-volatile acids,	..	..	241	..			..
Molecular weight of soluble volatile acids,	..		72	76	104		..

The blown oils chiefly produced for the manufacture of lubricants are blown rape oil, blown ravison oil, blown mustard oil, and blown cottonseed oil or 'lardine.' Cottonseed oil is the most easily thickened by blowing, but the blown oil is inferior as a lubricant to blown rape or mustard oils. Blown cottonseed oil is frequently more or less turbid, and deposits a sediment on standing. Blown cottonseed oil does not mix so freely with mineral oil as blown rape or mustard oil, and the miscibility of all oils becomes less the more they are blown. Blown oils mix more readily with Russian and Scotch than with American mineral oils.

TABLE XXVIA.—CHARACTERS OF COMMERCIAL BLOWN OILS

Description of Blown Oil.	Sp. Gr. at 60° F.	Free Acid (as Oleic).	Saponification Value.	Iodine Value.	Insoluble Fatty Acids.	Soluble Acid Value (KOH.)	Oxidized Fatty Acids.*	Apparent Acetyl Value.	True Acetyl Value.	Unsaponifiable Matter.
					Per cent.					
Rape,	0·9714	..	20·56	..	..	..	24·95	6·20	5·31	
,,	0·9674†	4·88†	20·75†	65·3†	88·64†	3·78†	..	.	..	
East Indian Rape	0·9023	6·62	21·56	61·9	82·18	5·63	20·74	10·29	4·66	0·93
Ravison,	0·9685	5·23	19·83	72·7	83·52	3·59	21·22	8·84	5·29	1·23
Cottonseed,	0·9722	..	21·37	..	..	..	26·45	6·56	4·85	..
,, ,,	0·9785	4·70	22·46	65·7	82·59	4·85	23·39	11·07	6·43	1·37

* Insoluble in petroleum spirit. † Gripper.

Blown oils in admixture with mineral oils are very largely used as lubricants; and for certain purposes, such as the lubrication of marine engines, such mixtures appear to supply a distinct want. The mineral oils entering into their composition are usually those of low or moderate viscosity. Whether such mixtures are as suitable for railway work as those produced by mixing mineral oils of greater viscosity with ordinary refined vegetable or animal oils, such as rape oil or tallow oil, has never been satisfactorily proved, so far as the authors are aware. Nevertheless, it is a fact that some large railway companies use one kind of mixture and some the other.

D.—ROSIN OIL.

Rosin oil is the principal product of the destructive distillation of common rosin or colophony. The distillation is conducted in cast-iron stills heated by a fire below. The charge of rosin varies from 3 to 10 tons. The first portion of the distillate, boiling between 80° and 250° C. (176° and 482° F.) and amounting to about $2\frac{1}{2}$° to 5 per cent. of the weight of the rosin, is a very complex, limpid liquid, known as resin spirit, which is used for making varnish and for the adulteration of oil of turpentine. This is followed, at a temperature above 300° C. (572° F.), by the rosin oil, which, if the distillation be pushed to dryness, may amount to 85 per cent. of the total products. About $2\frac{1}{2}$ per cent. of water containing a little acetic acid passes over during the distillation, and a considerable quantity of gas is given off, consisting of oxides of carbon, and hydrocarbons of the ethylene series.

A residue remains in the still, consisting of either pitch or coke, according to the stage at which the distillation is arrested.

Crude rosin oil is a viscid liquid of more or less dark brown colour, with a strong. usually blue or violet, fluorescence. It always contains a considerable proportion of rosin acids which have distilled over unchanged. By heating to a temperature of 150° C. (302° F.) for three or four hours, the last traces of spirit are removed, the oil loses from 1 to 5 per cent. in weight, and acquires a green fluorescence. By well boiling with water to expel acetic acid, and redistilling once or twice from caustic soda, refined rosin oils are obtained, which are pale in colour. The fluorescence or bloom is destroyed by exposing the oil to the air and sunlight in shallow vessels, or by treatment with hydrogen peroxide, nitro-naphthalene, etc.

Commercial rosin oils usually range in specific gravity, according to Lewkowitsch, from about 0·96 to 0·99, but oils are met with having a specific gravity as high as 1·01. Rosin oils are strongly dextrorotatory, the rotation varying from 30 to 40 degrees or more in a 100 mm. tube. These properties, their ready solubility in acetone, and certain colour reactions, are made use of to distinguish rosin oils from mineral oils (see p. 295).

Rosin oils, when titrated with alcoholic potash, neutralize an amount of alkali which varies according to the quantity of rosin acids they contain. According to Leeds,[1] the crude oils neutralize from 2·8 to 4·4 per cent. of potash (KOH), but by careful distillation or refining they can be obtained almost neutral. Esters or anhydrides are also present, which do not neutralize alkali in the cold, but can be saponified by boiling with potash, as in determining the saponification value (p. 221). The rosin acids can be obtained from 'he soap solution, gravimetrically, by acidifying and shaking with ether, after removing the neutral rosin oil as described in Chapter VII., p. 224 Owing to the presence of rosin acids, commercial rosin oil has the property of combining with calcium hydroxide and other bases, forming peculiar greasy bodies. This property is utilized in the manufacture of *rosin grease* (see p. 129).

The chemical composition of rosin oil is not fully known. According to Renard,[2] the neutral oil, purified from acid substances by washing with caustic soda solution, consists to the extent of about 80 per cent. of *diterebenthyl* ($C_{20}H_{30}$) boiling at 343°–346° C. (649°–655° F.); about 10 per cent. is *diterebenthylene* ($C_{20}H_{28}$), and about 10 per cent. *didecene* ($C_{20}H_{36}$). The hydrocarbon $C_{20}H_{30}$ obtained by Renard, when exposed to the air in thin layers for five days, absorbed about one-tenth of its weight of oxygen, and dried to a varnish.

Rosin oil is used as a lubricant for batching jute. It is not suitable for the lubrication of machinery, but is used to adulterate mineral and other lubricating oils. The methods for its detection are given in the chapters following.

[1] *Jour. Soc. Chem. Ind.* xi. (1892), p. 308.
[2] *Jour. Chem. Soc.*, 1888, Abs., p. 161.

E.—LUBRICANTS CONTAINING SOAP. GREASES.

Soap-thickened Oils.—Mineral oils are sometimes artificially thickened by dissolving soap in them. Aluminium soap is usually employed for this purpose. It is prepared by saponifying whale, cottonseed, or lard oil, or by neutralizing commercial oleic acid, with caustic soda, and pouring the solution of soda soap, gradually, into a solution of common alum, stirring all the time. Crude aluminium oleate separates out as an insoluble, gummy precipitate, which is pressed free from water and heated with about four times its weight of mineral oil until dissolved. The gelatinous material thus produced is sold for thickening oils under the names '*viscom*,' '*oil-pulp*' or '*thickener*,' '*gelatin*,' etc. A comparatively small quantity melted into a mineral oil will considerably increase its apparent viscosity.

Mineral oils thickened in this way can easily be recognized by the tendency to form threads when the oily cork is removed from the bottle, and by their peculiar non-homogeneous appearance, resembling a mixture of oil and jelly. The spurious viscosity rapidly diminishes when the oil is heated. Schweitzer regards this addition to mineral oils as pure adulteration, and states that experience has shown that in contact with water and steam the aluminium soap is precipitated and clogs the machinery. On the other hand, Bloede states that by the presence of aluminium soap the adherence of the lubricant to metal surfaces is much increased.

Aluminium soap is not the only soap used as a thickener. A sample of thickened oil analysed by one of the authors had the following composition:—

Russian mineral oil (0·909),	.	.		.	97·08
Neutral fixed oil,	.	.	.	.	·58
Fatty acids as soap, etc.,		.	.	.	1·97
Ash, chiefly CaCO₃,	.		.	.	·12
					99·75

In this case, about 2 per cent. of lime soap was the thickener used. The Russian oil, freed from soap by washing with hydrochloric acid, had a viscosity at 60° F., about three times that of refined rape oil. The 2 per cent. of soap made it so viscid at 60° F. that it would not flow through the viscometer. The sample had the appearance of a non-homogeneous mixture of jelly and oil, and formed threads in dropping.

Soap-thickened Greases.—Under this name may be included the various greases which consist of mineral oil thickened with sufficient soap to form, at ordinary temperatures, a consistent grease. The soaps usually employed for this purpose are lime, soda, or lead soaps, made with various fats and oils. I. J. Redwood [1] has described in detail a

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[1] *Lubricants, Oils, and Greases* (Spon).

process of manufacturing a grease of this kind from mineral oil, horse fat, and lime, from which the following is abbreviated.

The fat is melted in a steam-jacketed kettle provided with a mechanical stirrer, and is raised to a temperature of about 180° F. Cream of lime is then added in sufficient quantity to saponify the fat, the cover is put on, and the whole is boiled and stirred until saponification is complete and a little of the soap rubbed down in the palm of the hand exudes only a few minute drops of water. A portion of the mineral oil, at a temperature of about 190° F., is then slowly sprayed on to the soap in the kettle, and is thoroughly incorporated with it by continual stirring ; a further quantity of mineral oil is then sprayed in cold, until the desired consistency is reached. After continuing to stir for about half an hour longer, the still hot contents of the kettle are run off through a cooling pipe into a grinding mill, in which all lumps are reduced and the grease is made of a uniform smooth consistency. It is then packed in casks.

Redwood states that '*cup*' greases are usually thickened with a soap made from either horse fat, cottonseed oil, or rape oil, saponified with lime as above described. ' *Engine*' greases are thickened with a soap made from tallow oil or lard oil and caustic soda, and often contain neatsfoot oil, Japan wax, beeswax, etc., in addition. The latter greases are paler in colour and firmer in consistency than those made with lime soap. They frequently contain excess of caustic soda, which becomes converted into carbonate of soda and is liable to cut the bearings. All these greases may be scented with nitro-benzene, which is added when the grease is in the mill, for the purpose of disguising the fat used in making the grease ; it serves no useful purpose, but is rather detrimental than otherwise. These greases may also contain solid lubricants, such as graphite, talc, etc., or mere filling materials, such as barytes and chalk. The following are a few analyses of greases of this kind :—

TABLE XXVII.—*a*. LIME SOAP GREASES. (Axle Greases.)

	1.	2.	3.	4.	5.
Mineral oil (0·885–0·912),	81·8	72·5	73·4	72·0	74·5
Fixed oil or fat,	...	...	1·4	0·5	0·4
Fatty anhydrides,	8·7	11·1	12·1	17·6	17·6
Lime,	1·3	1·5	2·6	1·9	1·5
Water, by difference,	8·2	14·9	10·5	8·0	6·1*
	100·0	100·0	100·0	100·0	100·1

* Determined.

b. SODA SOAP GREASES,

		1.	2.	3.
Mineral oil (0·886–0·899),	.	55·00	70·93	42·81
Fixed oil or fat, . .	.	8·97	2·02	34·38
Soda soap (anhydrous), .		16·11	9·30	16·37
Sodium silicate, .	.	...	6·10	4·76
Sodium carbonate, .	.	3·19	...	...
Sodium sulphate, .	.	1·67	...	...
Water, by difference,	.	15·06	11·65	1·68
		100·00	100·00	100·00

c. LEAD SOAP GREASE.

Mineral oil (0·900), .	.	.	.	.	.	.	48·0
Neutral fat,	.	.	.	.	.	.	8·7
Fatty acids,	.	.	.	.	.	.	2·6
Resin acids,	.	.	.	.	.	.	9·9
Lead oxide,	.	.	.	.	.	.	3·0
Lime, .	.	.	.	.	.	.	0·9
Water, .	.	.	.	.	.	.	27·2
							100·3

Railway Wagon Grease.—The yellow grease used in the axle-boxes of railway wagons is composed, usually, of tallow, palm oil, soap, and water. Lant Carpenter states that a grease containing from 1·1 to 1·2 per cent. of soda has been found to give the best results. The tallow and palm oil are heated to 180° F. (82° C.), and a solution of the carbonate of soda in the water heated to 200° F. (93·5° C.) is allowed to flow into the melted oil; the whole is then well stirred together and run into large tubs to cool slowly. The following formulæ for greases of this kind are said to have stood the test of successful experiment :—

TABLE XXVIII.- FORMULÆ FOR RAILWAY WAGON GREASE.

Materials	Summer.	Medium.	Winter.
Tallow, ...	22·0	20·0	18·0
Palm oil, . .	12·0	12·0	2·0
Sperm or colza oil, .	1·0	1·5	2·0
Soda crystals, .	5·0	5·0	5·0
Water, . . .	60·0	61·5	63·0
	100·0	100·0	100·0

The soda crystals (sodium carbonate) in the above formulæ would have the effect of neutralizing and forming a more or less perfect soap with the free fatty acids contained in the palm oil and tallow, but it would probably be better, instead of adding a fixed weight of sodium carbonate, to add sufficient caustic soda to neutralize the free acid actually present in the fat used.

Sometimes a manufactured soap made from palm oil is used; thus, the grease used on the Midland Railway was formerly made by dissolving 6 cwt. of palm soap in twice its weight of water, and adding to the soap solution 6 cwt. of tallow and 2 cwt. of palm oil. The well-stirred mixture was run into shallow iron pans, in which it was stirred with wooden paddles until set. The palm oil is now replaced by a dark mineral oil, the process of manufacture remaining in other respects the same. The following is the percentage composition of this grease, allowing $2\frac{1}{2}$ per cent. for loss by evaporation of water during manufacture :—

Tallow, ...	23·3
Palm oil or mineral oil, ...	7·8
Dry soap, ...	16·3
Water, ...	52·6
	100·0

In an experiment made on the Great Western Railway in 1865, under the direction of Mr. Clayton, late Carriage and Wagon Superintendent of the Midland Railway, a train of passenger carriages lubricated with axle-grease ran 4999 miles in four weeks without replenishing the axle-boxes, and at the end of that time about 66 lbs. of grease had been used. This quantity was equivalent to 21 ounces of grease per 100 miles for the whole train, or $3\frac{1}{2}$ ounces for each carriage, or less than 1 ounce of grease per axle-box per 100 train miles.

A good wagon-axle grease should melt at 100°–110° F., without separating. Cup greases which melt at higher temperatures, and from which the mineral oil separates and leaves the soap, are unsuitable for railway wagons.

Wagon grease is sometimes adulterated with china clay. A sample examined by one of the authors contained

Fatty matter and soap, ...	20·8
China clay, ...	19·3
Water, ...	59·9
	100·0

Besides being a poor lubricant, this grease caused trouble through the china clay accumulating in the boxes.

Rosin Grease.—Rosin grease is made by stirring together rosin oil and slaked lime. One method of preparation consists in stirring the rosin oil with about three-fourths of its weight of slaked lime made into a cream with water. The mixture rapidly solidifies, ex-

pelling the superfluous water, which is run off, and the grease is
then diluted by gradually stirring in a further quantity of oil, until
the desired consistency is attained. The oil used for diluting may
be rosin oil, petroleum, or neutral coal-tar oil ('grease oil'). Grease
is also made by mixing dry slaked lime with rosin oil, without water,
also by mixing the lime with mineral or coal-tar oil, and adding the
rosin oil afterwards. Barytes, gypsum, whiting, and other filling
materials are also sometimes added.

I J. Redwood describes the following method of making a '*set*' or
axle-grease from rosin oil and mineral oil :— Dry sifted slaked lime
and twice its weight of mineral oil are thoroughly stirred together
for several hours, until a perfectly uniform mixture is produced. A
certain quantity of this prepared liquid, called the 'lime part,' is run
into a barrel or other receptacle, and, whilst being vigorously stirred
by means of a perforated metal disc attached to a handle, which is
worked up and down in the barrel, the rosin oil or 'set' is quickly
run in, and the whole is stirred for a few seconds and then allowed
to remain at perfect rest until thoroughly set, which will take place
in from five to fifteen minutes.

The formation of rosin grease has been attributed to a supposed
property possessed by the unsaturated hydrocarbons contained in
rosin oil of combining directly with lime and other bases. This,
however, is not the true explanation. Crude rosin oil invariably
contains a considerable percentage of rosin acids (undecomposed
colophony), which have distilled over with the hydrocarbons, and it
is the combination of these acids with the lime, forming a soap when
the rosin oil and the lime are stirred together, which is the real cause
of the formation of rosin grease. Refined rosin oil, which has been
freed from rosin acids, is incapable of forming a grease with lime ;
on the other hand, the larger the percentage of rosin acids contained
in the crude rosin oil, the stiffer the grease which can be formed.[1]

Rosin greases are used to lubricate the iron axles of colliery trucks
and ordinary road vehicles. They are not suitable for brass bearings,
on account of the rapidity with which the grease *acetines* under the
influence of heat and friction.[2] The composition of rosin grease is
shown by the following analyses :—

Hydrocarbon oil (0·954),	.	.	87·7
Rosin,	.	.	3·7
Slaked lime ($Ca(OH)_2$),	.	.	6·4
Water, by difference,	.	.	2·2
			100·0
Hydrocarbon oil (0·962),	.	.	86·6
Rosin,	.	.	7·0
Slaked lime ($Ca(OH)_2$),	.	.	4·5
Water, etc.,	.	.	1·9
			100·0

[1] Archbutt, *Jour. Soc. Chem. Ind.*, **xx.** (1901), p. 1193.
[2] Mills, *Destructive Distillation*, p. 98.

Even rosin grease is adulterated. One of the authors once examined a grease of this kind, sold for lubricating colliery trams, which contained nearly 50 per cent. of calcium sulphate and 25 per cent. of water.

Screwing and Drilling Liquids.—The liquid used for lubricating cutting tools is usually a solution in water of soft soap and soda. The liquid used at one works is made by boiling in 100 gallons of water 18·5 pounds of soda and 15·5 pounds of soft soap. Another lubricant of this kind was found by analysis to be a solution of rosin soap in rosin oil. It had the following composition :—

Rosin oil,	74·9
Rosin acids,	23·5
Soda (Na$_2$O),	1·5
Oxide of iron and lime,	·1
	100·0

Another liquid, which readily formed an emulsion with water, was composed of

Mineral oil,	54·2
Fixed oil,	1·4
Free fatty acids,	16·2
Soda and ammonia soaps,	11·7
Water,	16·5
	100·0

Hot-neck Greases.—These greases are frequently made from still residues, such as stearine pitch, wool pitch, mineral pitch from the distillation of American crude petroleum, Russian mineral pitch or goudron, either alone or mixed with heavy mineral lubricating oils, and thickened with rosin grease, soap, etc. Coal tar pitch and Trinidad pitch are also used. Some of the best hot-neck greases are composed of heavy mineral lubricating oils thickened with soap.

CHAPTER VI.

A.—VISCOSITY AND VISCOMETRY.

THE meaning of viscosity having been explained and the subject
discussed generally in Chapter II., the methods of measuring the
viscosities of oils and other liquids ('*viscometry*') will alone be
considered here. Various methods have been proposed, based upon
such observations as the rate of ascent of air-bubbles or hollow glass
spheres in the liquid ;[1] the torsional vibration of a disc in its own
plane when suspended by a wire and immersed in the liquid ;[2] the
speed of rotation of paddle wheels, cylinders, etc., immersed in the
liquid and kept in motion by a falling weight,[3] etc., etc. The most
accurate, and the most generally employed method for exact work, is
that of Poiseuille, in which the rate of flow of the liquid through a
capillary tube under known conditions of temperature and pressure
is measured. For commercial purposes the comparative viscosities of
lubricating oils are usually ascertained by measuring and comparing
the rates of discharge ('efflux velocities') of the oil and of some
standard liquid from a small orifice or jet ; in the United States,
however, Doolittle's Torsion Viscometer is a good deal used.

We shall commence with a description of the method of Poiseuille ;
for although that method has not come into general use for com-
mercial purposes, it has occasionally been thus employed, and we
have used it for determining the viscosities of mixtures of glycerol
and water from which the table on pp. 140–143 was constructed.

Absolute Viscometry.

Determination of Viscosity in Absolute Measure.[4]—Poiseuille's
method of viscometry depends upon the following facts, which he
proved experimentally :—(1), that the rate of flow of liquid through

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[1] Mills. See Redwood, *Petroleum*, first edition vol. ii. p. 619.
[2] Doolittle, *Jour. Amer. Chem. Soc.*, xv. (1893), p 173 ; and *Jour. Soc. Chem. Ind.*, xii. (1893), p. 709.
[3] Napier and Cockrell. See Redwood, *Petroleum*, first edition, vol. ii. p. 619.
[4] See p. 18.

a capillary tube of suitable dimensions is proportional to the pressure, and inversely proportional to the length of the tube ; and (2), that the rate of flow through a capillary tube of cylindrical bore is proportional to the fourth power of the radius of the bore. Prof. Osborne Reynolds has shown [1] that to ensure these conditions of steady viscous flow the proportions of the tube must be such that $\frac{r_0 \bar{v} d}{\eta}$ is less than 700, where r_0 is the radius of the bore, $\bar{r}$ the mean velocity of the fluid, d the density of the fluid, and η its viscosity. The viscosity of the fluid in absolute measure is then given, approximately, by Poiseuille's formula,

$$\eta = \frac{\pi g d h r_0^4 t}{8 V a},$$

in which g is the acceleration due to gravity, d the density of the fluid, h the mean head, t the time, V the volume of liquid discharged, and a the length of the tube.

To obtain the true viscosity, corrections must be made : (a) for the viscous resistance to the flow of the liquid at the ends of the tube ; (β) for the abnormal flow of the liquid on first entering the tube ; (γ) for the kinetic energy with which the liquid leaves the tube ; and (δ) for the resistance due to surface tension effects at the discharge orifice. Corrections a and β have never yet been devised, but errors due to these effects may be reduced to very small proportions by making the tube long. Correction γ is made by deducting from the mean head a quantity $= \frac{v^2}{g}$; this correction may be made very small by using a tube so narrow and so long that the movement of the liquid is very slow. The error due to surface tension effects, which may be serious, is so variable that the correction δ is best eliminated altogether by immersing the discharge orifice in the liquid and making a suitable deduction from the head.

Description of an Absolute Viscometer.—The apparatus employed by the authors is illustrated in fig. 37. The capillary tube A was carefully selected and calibrated from end to end, and was found to be of practically uniform bore. Viewed through a lens magnifying 20 diameters, the bore appeared to be perfectly cylindrical in section. The diameter, calculated from the weight of mercury required to fill the tube, was 0·6180 mm., and the length of the tube, measured by a Whitworth machine, was 21·991 cm. Thus, the length was about 350 times the diameter, and, as we estimate from experiments made with Redwood's viscometer that the magnitude of the correction a (see above) is about equal to the friction of a length of capillary tube equal to the diameter of the bore, our results from this cause cannot be more than about 0·28 per cent. too high. The kinetic energy correction, γ, also became very small, owing to the narrowness of the bore, amounting to only 0·5 per cent. of the head in the case of water (viscosity = 0·01), and being quite negligible in the case of all the glycerol solutions except the thinnest ($\eta = 0·0379$), and in that making a difference of only 0·05 per cent., or 2 in the fifth decimal place.
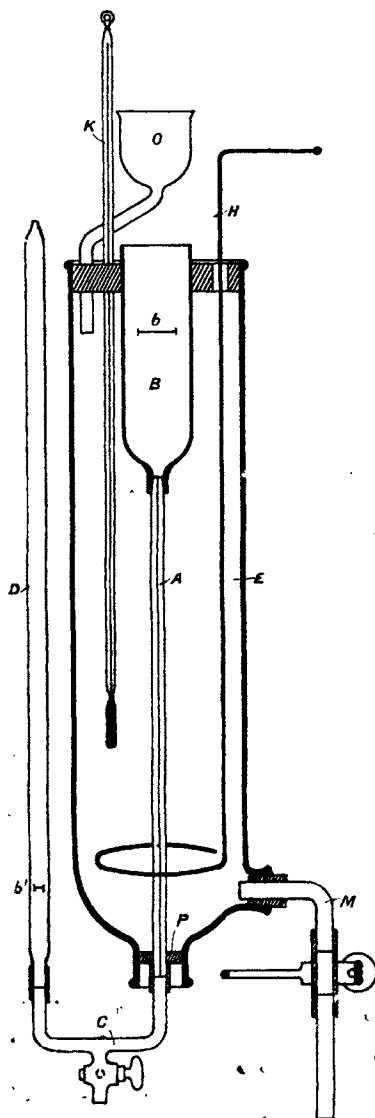
FIG. 37.

The capillary tube was ground into the neck of the reservoir B, and was connected at its lower end, through the wide glass tube C, with the measuring tube D. The glass water-jacket E for maintaining the temperature constant contained a stirrer of brass wire H and a thermometer K, indicating tenths of a degree Centigrade. By drawing off a little water through the tube M, and adding either warmer or colder water through the funnel tube O, and vigorously stirring, the slightest alteration in the temperature of the bath could be corrected at once. This is a most important point, for the viscosity even of water undergoes a remarkably rapid alteration with change of temperature. Thus, the viscosity of water, which is about 0·013 at 10° C., falls to 0·010 at 20°, or an average diminution of 2·3 per cent. per degree. The viscosity of oils, especially mineral oils, and of many other liquids, changes at a much greater rate. Bearing in mind the great importance of keeping the temperature of the liquid constant, the india-rubber disc P, closing the lower neck of the water-jacket, was made only about ¾ inch thick, and was pushed high up into the neck in order that the projecting end of the capillary tube below the water-line should be as short as possible and well screened from currents of cooler or warmer air. The tubes C and D, which were not part of the original design of the apparatus, were added in consequence of the erratic results obtained with water, owing to the varying tension of the free surface of the liquid (correction δ),

when the end of the capillary tube was open to the air. D was drawn out to a point at the upper end, in order to prevent, or reduce to a minimum, evaporation of, or absorption of, moisture from the air by the liquid in the tube. D was not jacketed ; but, as all our experiments with this apparatus were made at 20° C., which was very nearly the temperature of the laboratory, any error due to the very slight difference in the temperature, and therefore in the density, of the fluid in D as compared with that in B, must have been quite negligible. The tube D was carefully calibrated, and the capacity in c.c. per millimetre, from the zero mark b' upwards, was accurately ascertained. The reservoir B was also calibrated, from the zero mark b downwards. The vertical distance between the two zero marks, measured by a cathetometer, was 25·50 cm. The shaded portions of the figure represent indiarubber connections.

Method of Experiment.--The tube C was first of all disconnected from tubes A and D, and each was thoroughly well washed with water, then rinsed with alcohol and ether, and dried by aspirating air through it. Having filled B, A, and C, and moistened the inner surface of D with the liquid to be tested, C was again fixed in position, taking care that no air bubbles were entrapped, and that the ends of the tube were pushed into close contact with the ends of A and D. The height of D was then adjusted in the clamp holding it, so that the zero mark b' was exactly level with a fixed mark on the capillary tube A. The upper end of the capillary tube was closed, meanwhile, by a valve made of a small cork fixed on the end of a platinum wire. The liquid was allowed to remain at rest until the temperature had settled down to exactly 20° C., and during this time the free surfaces of the liquid in B and D were accurately adjusted to the zero marks. All being ready, and the liquid perfectly motionless, the cork valve was raised and the liquid allowed to flow ; the time was then measured which the meniscus in D took to rise between two points, the heights of which above b' were successively measured by a cathetometer. In experimenting with a thin liquid like water, the fluid rose in D with comparative rapidity, and after each experiment the valve was closed and the liquid readjusted to the zero marks ; but with the glycerin solutions the rise took place so slowly that several successive observations could be taken without stopping the flow of liquid. The excess of tension of the meniscus in the narrow tube D over that in the wide tube B was ascertained separately for each liquid by connecting D with a tube of the same diameter as B, without the intermediate capillary tube, and measuring with the cathetometer the difference in height of the liquid columns which balanced each other in the two tubes ; this difference was added to the measured head.

The apparatus, as shown in fig. 37, was found to give very good results with liquids whose viscosity did not exceed that of rape oil (about 1·11 at 60° F.). With more viscous fluids, the movement was so sluggish that it was found necessary to increase the pressure by lowering the tubes C and D and inserting a connecting tube between C and A. In these experiments, the head was measured by the cathetometer on a millimetre scale suspended vertically by the side of the apparatus.

Experimental Determination of the Viscosity of Water at 20° C.—This determination was made to test the capabilities of the apparatus and method of working. The distilled water used was well boiled in a silver flask to expel dissolved gases, cooled to 20° C., and immediately introduced into the viscometer.

t, the mean time of flow, was measured by a stop-watch, which was started and stopped as the meniscus in D passed two points, 2·155 cm. and 10·83 cm. respectively, above zero (b'). Five experiments were made,

and the times recorded were 136·2, 136·3, 135·8, 135·9, and 135·8 seconds; hence the mean time was *136·0 seconds.*

V, the volume of water flowing through the capillary tube in t seconds, was the capacity of D between the two points above referred to, and amounted to *4·00756 c.c.*

h, the mean head of water, was calculated by subtracting from the vertical distance bb' the initial and final distances of the liquid surfaces below b and above b', one centimetre of tube D being equal in capacity to 0·032 centimetre of B. Thus :—

Centimetres.

Initial head $= 25·50 - 2·155 - (2·155 \times 0·032) = 23·28$
Final head $- 25·50 - 10·83 - (10·83 \times 0·032) = 14·32$

Mean	$= 18·80$
Add excess tension of meniscus in D	·28

Mean head (h)	$= 19·08$

Subtract for kinetic energy of efflux (h^1)
$\dfrac{v^2}{g}$, where $v = \dfrac{V}{\pi r_0^2 t}$ (*Wilberforce*) $\Big\}$ $= \cdot098$

Corrected mean head $(h - h^1)$ $= 18·982$ cm.

d, the density of water at $\frac{20°}{4°}$ C.,	$=$	0·998259
r_0, the radius of the capillary tube,	$- -$	0·0309 cm.
a, the length of the capillary tube,	$=$	21·991 cm.
g, the acceleration due to gravity,	$=$	980·51 cm. seconds.
π,	$=$	3·14159

Then, by the formula (*Poiseuille-Wilberforce*)

$$\eta = \frac{\pi r_0^4 t g d (h - h^1)}{8 V a} = 0·01028.$$

Therefore, the absolute viscosity of water in C.G.S. units at 20° C. determined by this apparatus is 0·01028 dyne per sq. cm.[1]

Viscosities at 20° C. of Mixtures of Glycerol and Water.—The glycerin used for these determinations was purchased as pure from Messrs. Hopkin & Williams. The specific gravity at $\frac{20°}{20°}$ C. was 1·2568, corresponding to 98 per cent. of glycerol and 2 per cent. of water, according to Gerlach's table. The viscosity of this was carefully determined, without dilution. It was then mixed with distilled water. Six different mixtures were prepared, having a suitable range of viscosities, and the specific gravity and viscosity of each mixture were carefully determined. The data and results obtained are given in the following tables.

[1] Magnus Maclean (*Physical Units*, 1896) gives the value 0·0102, based upon results obtained by Sprung (1876), Meyer (1877), and Slotte (1883). Thorpe and Rodger (*Phil. Trans.*, vol. clxxxv.A, p. 397) obtained the value 0·010015, and have recalculated the values obtained by previous observers with the following results :—Poiseuille, 0·01008 ; Sprung, 0·01003 ; Slotte, 0·01008.

TABLE XXIX.—VISCOSITIES IN DYNES PER SQ. CM. OF MIXTURES OF GLYCEROL AND WATER.

GLYCERIN No. 1.—Specific gravity at $\dfrac{20°}{20°}$, 1·1007

,, ,, $\dfrac{20°}{4°}$, 1·0988

Glycerol = 40·0 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds	Viscosity (η).
1	0·9298	22·51	89·3	0·0379
2	1·3809	17·87	167·8	0·0381
3	2·7868	21·48	278·7	0·0377
4	3·7052	20·45	390·1	0·0378

GLYCERIN No. 2.—Specific gravity at $\dfrac{20°}{20°}$, 1·1848

,, ,, $\dfrac{20°}{4°}$, 1·1828

Glycerol = 71·04 % (*Gerlach*).

Number of Experiment	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η)
1	0·9297	22·75	511·6	0·2364
2	0·9298	20·17	574·1	0·2351
3	0·9188	17·59	654·2	0·2365

GLYCERIN No. 3.—Specific gravity at $\dfrac{20°}{20°}$, 1·2057

,, ,, $\dfrac{20°}{4°}$, 1·2037

Glycerol = 78·78 % (*Gerlach*).

	Number of Experiment.	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η).
1st Series.	1	0·4647	23·47	518·2	0·5029
	2	0·4651	21·92	549·1	0·4972
	3	0·4652	20·37	579·4	0·4875
2nd Series.	4	0·6975	22·03	917·6	0·4962
	5	0·6973	19·97	905·3	0·4982
	6	0·6895	17·91	1014·2	0·5062

G<small>LYCERIN</small> No. 4.—Specific gravity at $\frac{20°}{20°}$, 1·2155

" " $\frac{20°}{4°}$, 1·2134

Glycerol = 82·41 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η).
1	0·4644	24·61	729·3	0·7486
2	0·6971	23·22	1165·6	0·7520
3	0·6977	21·36	1262·5	0·7486

G<small>LYCERIN</small> No. 5.—Specific gravity at $\frac{20°}{20°}$, 1·2240

" " $\frac{20°}{4°}$, 1·2218

Glycerol = 85·55 % (*Gerlach*).

	Number of Experiment.	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η).
1st Series.	1	0·4645	24·12	1099·9	1·1142
	2	0·6973	22·62	1742·0	1·1024
2nd Series.	3	0·4649	22·26	1193·0	1·1144
	4	0·4652	21·02	1258·0	1·1089
	5	0·4646	19·77	1345·0	1·1166

G<small>LYCERIN</small> No. 6.—Specific gravity at $\frac{20°}{20°}$, 1·2463

" " $\frac{20°}{1°}$, 1·2444

Glycerol = 93·96 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η)
1	0·4645	98·63	969	4·0861
2	0·4649	97·19	980	4·0687
3	0·4652	95·43	1001	4·0779
4	0·4640	93·99	1015	4·0832

TABLE XXIX.—*continued.*

GLYCERIN No. 7.—Specific gravity at $\frac{20°}{20°}$, 1·2568

  ,,   ,, $\frac{20°}{4°}$, 1·2546

Glycerol = 98·0 % (*Gerlach*).

Number of Experiment.	Volume (V) c.c.	Mean Head (h) cm.	Time (t) Seconds.	Viscosity (η)
1	0·4644	99·25	2030	8·6884
2	0·4648	97·70	2051	8·6337
3	0·4650	96·46	2103	8·7366

COLLECTED RESULTS AND MEAN VALUES.

GLYCEROL AND WATER.—Viscosity at 20° C.

Sp. gr. at $\frac{20°}{20°}$	1·1007	1·1848	1·2057	1·2155	1·2240	1·2463	1·2568
,, ,, $\frac{20°}{4°}$	1·0988	1·1828	1·2037	1·2134	1·2218	1·2441	1·2546
Glycerol % (*Gerlach*)	40·0	71·04	78·78	82·41	85·55	93·96	98·0
	0·0379	0·2364	0·5029	0·7486	1·1142	4·0861	8·6884
	0·0381	0·2351	0·4972	0·7520	1·1024	4·0687	8·6337
η	0·0377	0·2365	0·4875	0·7486	1·1144	4·0779	8·7366
	0·0378	...	0·4962	...	1·1089	4·0932	...
	...	...	0·4982	...	1·1166	...	...
	...	...	0·5062	...	...	...	...
Mean values of η	0·0379	0·2360	0·4980	0·7497	1·1113	4·0790	8·6862

The logarithms of the mean values of η in the above table of collected results were plotted upon a diagram as ordinates, and the specific gravities at $\frac{20°}{20°}$ as abscissæ. It was found that a very regular curve could be drawn through the seven points, confirming the general accuracy of the results. By means of this curve the lengths of the ordinates corresponding to specific gravities ranging from 1·00 to 1·262 were carefully measured, and gave the values of the corresponding logs. of η to three decimal places. On tabulating these logs. it was found that the increment was not quite regular, owing to the unavoidable irregularity of the curve as drawn. A

systematic correction was, therefore, made which, while not altering the values of the logs. beyond the possible errors of experiment, made the increment a regular one. The corrected logs. thus obtained are given in Table XXX., with the corresponding viscosities to four figures.[1]

TABLE XXX. —VISCOSITIES, IN DYNES PER SQ. CM., OF MIXTURES OF GLYCEROL AND WATER.

Sp. Gr. at $\frac{20°}{20°}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.	Sp. Gr. at $\frac{20°}{20°}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.
1·000	·01028	2·01183	520	1·032	·01513	2·17992	532
1·001	·01040	2·01703	520	1·033	·01532	2·18525	533
1·002	·01053	2·02223	521	1·034	·01551	2·19058	533
1·003	·01065	2·02744	521	1·035	·01570	2·19592	534
1·004	·01078	2·03265	521	1·036	·01590	2·20127	535
1·005	·01091	2·03786	521	1·037	·01609	2·20663	536
1·006	·01104	2·04307	522	1·038	·01629	2·21200	537
1·007	·01118	2·04829	522	1·039	·01650	2·21738	538
1·008	·01131	2·05351	522	1·040	·01670	2·22277	539
1·009	·01145	2·05873	522	1·041	·01691	2·22817	540
1·010	·01159	2·06395	523	1·042	·01712	2·23358	541
1·011	·01173	2·06918	523	1·043	·01734	2·23900	542
1·012	·01187	2·07441	523	1·044	·01756	2·24443	543
1·013	·01201	2·07964	524	1·045	·01778	2·24987	544
1·014	·01216	2·08488	524	1 016	·01800	2·25532	545
1·015	·01231	2·09012	524	1·047	·01823	2·26078	546
1·016	·01246	2·09536	525	1·048	·01846	2·26625	547
1·017	·01261	2·10061	525	1·049	·01870	2·27173	548
1·018	·01276	2·10586	526	1·050	·01893	2·27722	549
1·019	01292	2·11112	526	1·051	·01917	2 28272	550
1·020	·01307	2·11638	527	1·052	·01942	2 28823	551
1·021	·01323	2·12165	527	1·053	·01967	2 29375	552
1·022	·01339	2·12692	528	1·054	·01992	2·29928	553
1·023	·01356	2·13220	528	1·055	·02018	2·30482	554
1·024	·01372	2·13748	529	1·056	·02044	2·31037	555
1·025	·01389	2·14277	529	1·057	·02070	2·31593	556
1·026	·01406	2·14806	530	1·058	·02097	2·32150	557
1·027	·01424	2·15336	530	1·059	·02124	2·32708	558
1·028	·01441	2·15866	531	1·060	·02151	2·33267	559
1·029	·01459	2·16397	531	1·061	·02179	2 33827	560
1·030	·01477	2·16928	532	1·062	02207	2 34389	562
1·031	·01495	2·17460		1·063	·02236	2·34953	564

[1] Schottner (Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften Wien, vol. lxxvii. (1878) p 682, and vol. lxxix. (1879), found the viscosity of pure glycerol at 20° C. = 8·304, but as he states the specific gravity at 20° C. = 1·2516 the correctness of his result is open to question. Schottner's figures for dilute glycerin do not fall on any regular curve, and we have been unable to make any use of them.

TABLE XXX.—VISCOSITIES, IN DYNES PER SQ CM., OF MIXTURES OF GLYCEROL AND WATER— *continued*.

Sp. Gr. at $\frac{20°}{20°}$ C.	Viscosity at 20° C (η).	Log of Viscosity.	Differences.	Sp. Gr. at $\frac{20°}{20°}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.
1·064	·02266	2·35519	566	1·109	·04302	2·63369	684
1·065	·02296	2·36087	568	1·110	·04371	2·64057	688
1·066	·02326	2·36657	570	1·111	·04441	2·64749	692
1·067	·02357	2·37229	572	1·112	·04513	2·65445	696
1·068	·02388	2·37803	574	1·113	·04586	2·66146	701
1·069	·02420	2·38379	576	1·114	·04662	2·66852	706
1·070	·02452	2·38957	578	1·115	·04738	2·67563	711
1·071	·02485	2·39537	580	1·116	·04817	2·68279	716
1·072	·02519	2·40119	582	1·117	·04898	2·69000	721
1·073	·02553	2·40703	584	1·118	·04980	2·69726	726
1·074	·02588	2·41289	586	1·119	·05065	2·70457	731
1·075	·02623	2·41877	588	1·120	·05152	2·71193	736
1·076	·02659	2·42467	590	1·121	·05240	2·71935	742
1·077	·02695	2·43059	592	1·122	·05331	2·72683	748
1·078	·02732	2·43653	591	1·123	·05425	2·73437	754
1·079	·02770	2·44249	596	1·124	·05520	2·74197	760
1·080	·02809	2·44847	598	1·125	·05619	2·74963	766
1·081	·02848	2·45447	600	1·126	·05719	2·75735	772
1·082	·02887	2·46049	602	1·127	·05823	2·76513	778
1·083	·02928	2·46653	601	1·128	·05929	2·77298	785
1·084	·02969	2 47259	606	1·129	·06038	2·78090	792
1·085	·03011	2·47867	608	1·130	·06150	2 78889	799
1·086	·03053	2 48478	611	1·131	·06265	2·79695	806
1·087	·03097	2·49092	614	1·132	·06384	2·80508	813
1·088	·03141	2 49709	617	1·133	·06506	2·81328	820
1·089	·03186	2·50329	620	1·134	·06631	2·8'156	828
1·090	·03232	2·50952	623	1·135	·06760	2·82992	836
1·091	03279	2·51578	626	1·136	·06892	2·83836	844
1 092	·03327	2·52207	629	1·137	·07029	2·84688	852
1·093	·03376	2·52839	632	1·138	·07169	2·85548	860
1·094	·03426	2·53474	635	1·139	·07314	2·86416	868
1 095	·03476	2·54112	638	1·140	·07463	2·87292	876
1·096	·03528	2·54753	641	1·141	·07617	2·88177	885
1·097	·03581	2·55397	644	1·142	·07775	2·89071	894
1·098	·03635	2·56044	6·7	1·143	·07939	2·89974	903
1·099	·03689	2·56694	650	1·144	·08107	2·90886	912
1·100	·03745	2·57347	653	1·145	·08281	2·91807	921
1·101	·03802	2·58003	656	1·146	·08460	2·92737	930
1·102	·03860	2·58662	659	1·147	·08645	2 93676	939
1·103	·03920	2·59321	662	1·148	·08836	2·94625	949
1·104	·03980	2·59989	665	1·149	·09033	2·95584	959
1·105	·04042	2·60657	668	1·150	·09237	2·96553	969
1·106	·04105	2·61329	672	1·151	·09448	2·97532	979
1·107	·04169	2·62005	676	1·152	·09665	2·98521	989
1·108	·04235	2·62685	680	1·153	·09890	2·99520	999

TABLE XXX.—VISCOSITIES, IN DYNES PER SQ. CM., OF MIXTURES OF GLYCEROL AND WATER—continued.

Sp. Gr. at $\frac{20°}{20°}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.	Sp. Gr. at $\frac{20°}{20°}$ C.	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.
1·154	·1012	1·00529	1009	1·199	·3856	1·58608	1600
1·155	·1036	1·01548	1019	1·200	·4002	1·60224	1616
1·156	·1061	1·02578	1030	1·201	·4155	1·61857ᵃ	1633
1·157	·1087	1·03619	1041	1·202	·4316	1·63507	1650
1·158	·1114	1·04671	1052	1·203	·4485	1·65174	1667
1·159	·1141	1·05734	1063	1·204	·4662	1·66858	1684
1·160	·1170	1·06808	1074	1·205	·4848	1·68559	1701
1·161	·1199	1·07893	1085	1 206	·5044	1·70277	1718
1·162	·1230	1·08989	1096	1·207	·5250	1·72013	1736
1·163	·1262	1·10096	1107	1·208	·5466	1·73767	1754
1·164	·1295	1·11215	1119	1·209	·5694	1·75539	1772
1·165	·1329	1·12346	1131	1·210	·5933	1·77330	1791
1·166	·1364	1·13489	1143	1·211	·6186	1·79140	1810
1·167	·1401	1·14644	1155	1·212	·6452	1·80969	1829
1·168	·1439	1·15811	1167	1·213	·6733	1·82818	1849
1·169	·1479	1·16990	1179	1·214	·7029	1·84687	1869
1·170	·1520	1·18181	1191	1·215	·7341	1·86577	1890
1·171	·1563	1·19384	1203	1·216	·7672	1·88488	1911
1·172	·1607	1·20600	1216	1·217	·8021	1·90421	1933
1·173	·1653	1·21829	1229	1·218	·8390	1·92376	1955
1·174	·1701	1·23071	1242	1·219	·8781	1·94354	1978
1·175	·1751	1·24326	1255	1·220	·9195	1·96356	2002
1·176	·1803	1·25594	1268	1·221	·9635	1·98383	2027
1·177	·1857	1·26875	1281	1·222	1·010	·00436	2053
1·178	·1913	1·28169	1294	1·223	1·060	·02516	2080
1·179	·1971	1·29476	1307	1·224	1·112	·04624	2108
1·180	·2032	1·30796	1320	1·225	1·168	·06761	2137
1·181	·2096	1·32130	1334	1·226	1·228	·08928	2167
1·182	·2162	1·33478	1348	1·227	1·292	·11126	2198
1·183	·2231	1·34840	1362	1·228	1·360	·13356	2230
1·184	·2302	1·36216	1376	1·229	1·433	·15619	2263
1·185	·2377	1·37606	1390	1·230	1·511	·17916	2297
1·186	·2455	1·39010	1404	1·231	1·594	·20248	2332
1·187	·2537	1·40428	1418	1·232	1·683	·22616	2368
1·188	·2622	1·41860	1432	1·233	1·779	·25021	2405
1·189	·2711	1·43307	1447	1·234	1·882	·27464	2443
1·190	·2803	1·44769	1462	1·235	1·993	·29946	2482
1·191	·2900	1·46246	1477	1·236	2·112	·32468	2522
1·192	·3002	1·47738	1492	1·237	2·240	·35031	2563
1·193	·3108	1·49245	1507	1·238	2·379	·37636	2605
1·194	·3219	1·50767	1522	1·239	2·528	·40284	2648
1·195	·3335	1·52304	1537	1·240	2·690	·42976	2692
1·196	·3456	1·53856	1552	1·241	2·865	·45711	2735
1·197	·3583	1·55424	1568	1·242	3·054	·48488	2777
1·198	·3716	1·57008	1584	1·243	3·259	·51306	2818

TABLE XXX.—VISCOSITIES, IN DYNES PER SQ. CM., OF MIXTURES OF GLYCEROL AND WATER—*concluded*.

Sp. Gr. at $\frac{20°}{20°}$ C	Viscosity at 20° C. (η).	Log. of Viscosity.	Differences.	Sp. Gr at $\frac{20}{20°}$ C.	Viscosity at 20 C (η).	Log of Viscosity	Differences.
1·244	3·481	·54164	2858	1·251	7·043	·84778	3218
1·245	3·721	·57061	2897	1·255	7·591	·88029	3251
1·246	3·981	·59996	2935	1 256	8·187	·91313	3284
1·247	4·263	·62969	2973	1·257	8·837	·94630	3317
1·248	4·569	·65979	3010	1·258	9·546	·97980	3350
1·249	4·901	·69025	3046	1·259	10·32	1·01363	3383
1·250	5·261	·72107	3082	1 260	11·16	1·04779	3416
1·251	5·653	·75224	3117	1·261	12·09	1·08228	3449
1·252	6·078	78375	3151	1·262	13·10	1·11710	3482
1·253	6·540	·81560	3185				

Commercial Viscometry.

A very rough idea of the relative viscosity of an oil may be formed by shaking it in a bottle and observing the rate at which air-bubbles rise in the oil ; the more sluggish the movement of equal-sized bubbles, the greater the viscosity of the oil.

A rough quantitative method is to fill a 10 c.c. pipette with the oil, fix it in a vertical position in a clamp and count the number of seconds occupied by the oil in flowing from a mark on the upper stem to another mark on the lower stem. Then clean the pipette with ether, dry it, and make another similar experiment with some standard oil, say rape. For the results to be at all comparable, the oils must be at the same temperature when the experiment is made. To ensure this, small beakers containing 20 to 30 c.c. of each oil should be allowed to stand on a table, side by side, for an hour before making the test ; the pipette may then be filled from each beaker in succession. As a rough test for sorting quickly a number of samples of oil, this is useful, but for accurate work a properly constructed viscometer must be employed.

J. G. A. Rhodin[1] determines the viscosities of oils by means of a simple form of absolute viscometer, in which the formation of drops is the basis of observation. The period of time required for the fall of 30 drops is noted, and the drops are carefully weighed. From the weight of a single drop, the very small counter-pressure due to the surface tension of the drops is calculated and allowed for. Rhodin finds the weight of the drops from a perfectly clean tube remarkably constant. Thus, in two experiments 30 drops weighed, respectively,

[1] Private communication.

1·2220 grammes and 1·2214 grammes. The capillary tubes used have the following dimensions, viz.:—

1. $\begin{cases} r_0 = & 0\cdot83502 \text{ mm.} \\ l = & 386\cdot9 \text{ ,,} \end{cases}$ for $t = 15°$ C.

2. $\begin{cases} r_0 = & 0\cdot55322 \text{ ,,} \\ l = & 401\cdot7 \text{ ,,} \end{cases}$ for $t = 100°$ C.

The head is read off by means of a cathetometer. The following results show the accuracy attainable in duplicate experiments, the head varying in each experiment :—

Description of Oil	American Mineral Oil (·9106).	"Valvoline" Oil (·876).	Cylinder Oil.	Cylinder Oil.
Temperature .	15° C.	15° C.	100° C.	100° C.
Value of η—				
(1) . . .	2·2743	1·836	0·3406	0·2424
(2) . . .	2·2949	1·804	0·3403	0·2417
(3) . . .	2·2812	...	...	...

Rhodin finds the method simple and accurate, and it has the advantage of giving absolute instead of arbitrary results. The only drawback is the somewhat lengthy calculation, but this can be curtailed by adopting a uniform method of observation.

The viscometers mostly used for practical laboratory work have very short efflux tubes of comparatively wide bore. From these instruments a running can be made in a short space of time, and the parts are easily cleaned and kept in order. But the rate of efflux is far from being proportional to the viscosity of very fluid liquids and water, though in the case of lubricating oils having a viscosity at least as great as that of sperm oil at 60° F. (0·42), the error does not exceed about 2 per cent. The best known instruments of this class are Redwood's, which is the standard instrument in this country, Engler's and Kunkler's, which are used on the Continent, and Saybolt's, used in the United States. There are many others, but we do not think it necessary to describe them all. The glass viscometer devised by Coleman and improved by Archbutt is one of the most simple for practical purposes. It will be described as the Coleman-Archbutt viscometer. Doolittle's Torsion Viscometer will also be described.

Redwood's Standard Viscometer.—*Construction.*—This instrument, fig. 38, consists of a silvered copper cylinder A, about 1⅞ inches in internal diameter and 3½ inches deep, having a thick metal bottom, slightly concave the inside, in the centre of which the agate jet, J, is fixed. In the ument used by the authors the passage drilled through the jet is 12

millimetres in length, and very nearly 1·7 millimetres in diameter. *Slight* unavoidable variations in the jets of different instruments, causing a few seconds' difference in the rate of flow, are corrected by slightly varying the height of the pointed stud B, which determines the initial head of the oil. A small brass ball-valve fixed to a wire V, when resting in the hemispherical cavity in the agate jet, closes the orifice ; when raised so as to allow the oil to flow out, it is suspended, by a small hook, from the stud S. The cylinder A is fixed, by means of a screw thread and leather washer, in the centre of
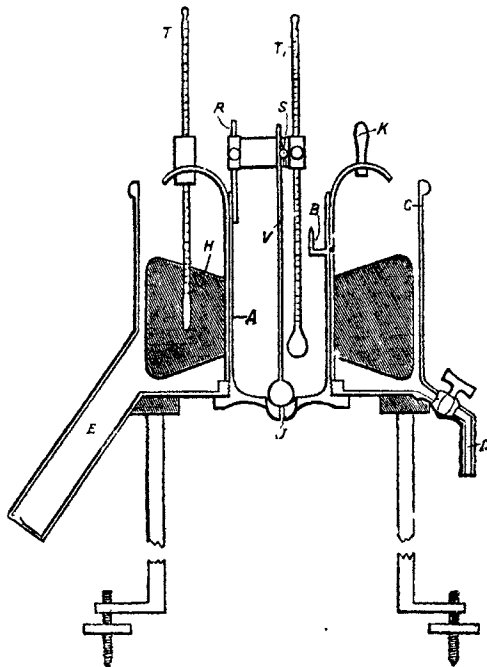
FIG. 38.

the brazed copper vessel C, which is furnished with a tap, D, and a copper heating tube E, projecting at an angle of 45° from the side, close to the bottom. This vessel contains water or oil, by means of which the temperature of the oil in A is maintained constant, and is provided with a stirring apparatus consisting of four light metal vanes, H, fixed to a thin copper tube which revolves smoothly round the cylinder A, the tube having a broad curved flange at the top to prevent any of the liquid in C from being splashed into the oil in A. The stirrer is rotated to and fro by means of the handle K, and carries with it the thermometer T, which registers the temperature of the fluid bath. Another thermometer, T₁, held by a spring clamp which

10

slides on the rod R, is immersed in the oil undergoing test. The instrument is supported on a tripod stand furnished with levelling screws.

Method of Experiment.—The interior of the cylinder A and the orifice of the jet are first inspected. They must be perfectly clean, dry, and free from any loose particles which might obstruct the free flow of the oil. In examining the interior, a small mirror held below is useful. After inspection, the instrument is levelled. The outer vessel, C, is then filled with water or heavy mineral oil, according to the temperature at which the viscosity is to be determined, water being used for all temperatures up to about 200° Fahr. The height of the liquid in C should be slightly above that of the oil in A. The temperature of the water-bath, having been adjusted, is maintained constant during the test by continual stirring, the thermometer being closely watched, and any tendency of the mercury to rise or fall corrected by additions of colder or warmer water, the excess of water being drawn off through the tap D. Temperatures much above the normal are maintained by heating the tube E, by means of a gas or spirit flame. The oil to be tested, if quite clear and bright, is next poured into A until the point of the stud B is just covered, the jet being first closed by the valve; if the oil be not clear, or if it be a dark-coloured oil, it must first of all be strained through fine wire gauze or muslin. Thick oils may be warmed before straining, but they must not be heated more than a few degrees above the temperature at which the test is to be made. The oil should be brought to nearly the required temperature before being poured into the viscometer, because the adjustment afterwards takes place slowly. The thermometer T_1 is immersed in the oil to such a depth that the bulb does not become uncovered during the test, and it is not afterwards moved. A narrow-necked flask, holding 50 c.c. to a mark on the neck, is placed below the jet to receive the oil. If the test is to be made at a temperature more than a few degrees above or below that of the air of the room, the flask must be immersed in a bath of liquid heated to the testing temperature, or the body of the flask may be surrounded by a thick layer of cotton-wool contained in a beaker, the neck and graduation-mark being left exposed to view. As there is generally a slight leakage from the valve, V, the flask should not be placed in position until the last moment.

When *both* thermometers register the desired temperature, the height of the oil in A is finally adjusted so that the point of the stud B lies exactly in the surface, and the measuring flask is placed under the jet. The valve V is then raised, a stop-watch being started at the same moment, and the number of seconds occupied in filling the flask up to the 50 c.c. mark is ascertained. This completes the test. In important cases, and always if the operator be inexperienced, the oil should be poured back into A, a little more being added to bring it up to the mark, and the test repeated, the measuring flask being first rinsed out with ether and dried. Duplicate tests ought not to differ more than 1 per cent.; greater differences will probably be due to neglecting to maintain a constant temperature.

Method of Standardizing.—This instrument is standardized with refined rape oil; but, as different samples of genuine rape oil vary in viscosity, Redwood has proposed the adoption of the arbitrary number 535, which is the average number of seconds required by 50 c.c. of rape oil to flow out of his viscometer at 60° F. The relative viscosity, at $x°$ F. of any oil, compared with the viscosity at 60° F. of rape oil of density 0·9142,[1] which is taken as 100, is then found by the following formula :—

$$\text{Relative viscosity (rape oil at } 60° \text{ F.} = 100) = \frac{td \ 100}{535 \times 0·9142},$$

[1] $= $ Sp. gr. 0·915 at $\dfrac{60°}{60°}$ F.

where t is the number of seconds required for the outflow of 50 c.c. of the oil at $x°$ F., and d is the density of the oil at the same tempe ature.

It will be observed that Redwood compares oils at all temperatures with rape oil at 60° F. · some prefer to make the comparison with both oils at the same temperature.

The 'Coleman-Archbutt Viscometer.[1]—This instrument, fig. 39, is an improved form of the well-known jacketed glass viscometer first used by Coleman about 1869.[2] It consists of a glass burette contained in an outer jacket, with a funnel for pouring in hot or cold water, a tube for running off water, and a stirrer for thoroughly mixing the water in the jacket. Being made of glass it is fragile ; but, with reasonable care an instrument may last for many years. It may be standardized with glycerin (see p. 156) so as to give results in absolute measure, and it has the advantage of being very convenient to work with. Thus, the temperature of the oil can be readily adjusted in the efflux-tube itself, by stirring with a thermometer and raising or lowering the temperature of the water in the outer jacket ; there is no need for a separate measuring vessel, the volume of oil which flows out being measured by marks on the efflux-tube ; a test can be made with as little as 25 c.c. of oil ; and after the test has been made the tube is empty and ready for the next test. Oils can be tested in this apparatus at the temperature of boiling water, which is high enough for most purposes.

Construction.—The efflux-tube A is about 15 inches in length. The upper 12 inches is made of thin-walled glass tubing, about 1 inch in internal diameter ; it then narrows to a diameter of about $\frac{3}{8}$ inch for 2 inches, and terminates in a thick-walled jet, about 1 inch long and of such internal diameter (about 1·9 mm.) that 100 c.c. of refined rape oil at 60° F. take about ten minutes to run out. If the oil runs too quickly, the orifice of the jet may be slightly closed by fusing the edges in the flame ; if too slowly, the jet may be shortened a little. Four circumferential marks are etched upon the tube. The lowest or zero mark is rather above the middle of the narrow portion ; the other three marks are on the wide portion, and divide the tube above the zero mark into capacities of 25 c.c., 5° c.c. and 100 c.c. The volume of oil used for a test may, therefore, be varied, according to the viscosity and the quantity of oil available. Of fairly fluid oils, *e.g.*, rape or machinery oils at 60° F., and all oils at 212° F., 100 c.c. are used , of more viscous oils, *e.g.* cylinder oils at 60° F. and 100° F., 25 c.c. is a suitable quantity. The tube must be separately standardized from each mark, as the times of efflux of the different volumes bear no simple relation to each other.

The outer jacket, J, is about 3½ inches in external diameter, and has a short narrow neck at the bottom and another at the side. The tube, A, is fixed in the jacket by means of a thick indiarubber bung at the top and a thin disc of rubber, not more than $\frac{3}{8}$ inch thick, at the bottom, through which the jet projects not more than $\frac{3}{8}$ inch. Thus, the oil in the tube is surrounded by the water in the jacket until it has reached nearly to the end of the jet, and the temperature is maintained constant until the oil has passed out of the tube. The jet is protected from change of temperature, as well as from fracture, by being contained entirely within the neck of the jacket. The large bung at the top is perforated by four small holes. One, which is lined with a short piece of glass tube, is for the brass stirring-wire S ; another is for the glass funnel F, which fits rather loosely, and is replaced by a tube L, conveying steam from the boiler B,[3] for determinations at

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[1] Made by Messrs. Baird & Tatlock.
[2] *Jour. Soc. Chem. Ind.*, v. (1886), p. 359.
[3] In the figure this tube is shown in dotted lines.
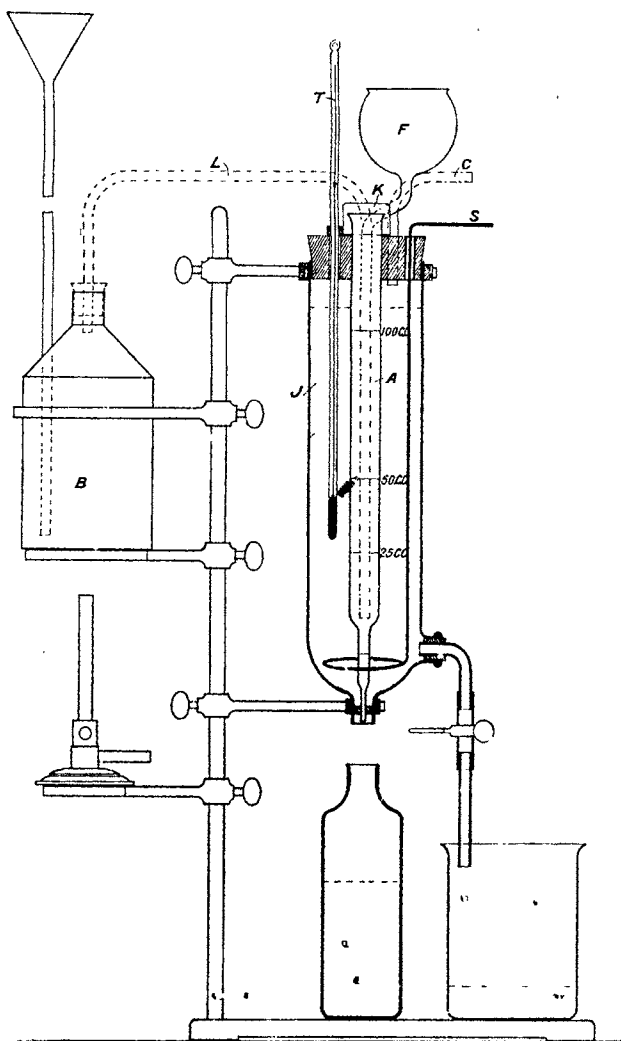
FIG. 39.—The Coleman-Archbutt Viscometer.

212° F. ; a third hole is for the bent tube C, for the escape of steam, and the fourth is for the thermometer T.

In putting the apparatus together, the tube A is first wetted and passed through the central hole of the bung, far enough for the jet to reach nearly to the end of the lower neck when the bung is fixed in the jacket ; the brass stirring-wire, S, which terminates in a brazed ring at the lower end, is then passed through its hole and bent over at the top to form the handle ; the bung is then carefully inserted into the jacket, and the jet is pushed through the disc of rubber at the lower end. Finally, the tube C is inserted in the bung.

Method of Experiment.—The tube A and jet are first carefully cleaned and dried ; the jet is then closed by means of a small peg of soft wood. Water at the proper temperature is next poured into the jacket, and the oil, previously strained, if necessary, and brought to the same temperature, is poured into the efflux-tube up to about half an inch above the mark it is intended to run it from. The oil is stirred with the thermometer, avoiding the formation of air-bubbles, until the temperature is exactly correct, the final adjustment being easily made by slightly raising or lowering the temperature of the water-bath. The thermometer is then taken out of the oil, which is allowed to rest until perfectly quiescent. The wood peg is then withdrawn, and the time taken by the oil to flow down to the zero mark is measured by a stop-watch, which is started as the surface of the oil passes the upper mark. During the experiment, the temperature is maintained constant by pouring hot or cold water into the jacket, through the funnel, and running off the excess through the side tube as often as required, using the stirrer frequently. The temperature of the water in the outer jacket is indicated by the thermometer, T, which is not removed. The open end of the efflux-tube is covered by the inverted beaker, K, to prevent water from being splashed in by the stirrer.

In making an experiment at 212° F., the cold water in the jacket is first raised gradually to about 180° F., by pouring in hot water, and then the funnel is replaced by the steam tube, L, and steam is blown in from the boiler. When the water boils, the level is lowered sufficiently to prevent splashing, and a brisk ebullition is kept up throughout the test The oil, previously heated to 212° F., should be poured in just before the water begins to boil, and the tube A covered by its cap.

Method of Standardizing.—If the relative viscosity of an oil be required, compared with, say, refined rape oil as the standard, the number of seconds occupied by the oil in flowing out is divided by the number of seconds occupied by the same volume of rape oil in flowing out at the same temperature, a correction being made for the difference in density of the oils. Thus,

$$\text{Relative viscosity} = \frac{td}{t_1 d_1} \times 100,$$

where t and t_1 are the respective times of flow, and d, d_1 are the respective densities of the oils referred to water at 4° C.

For the method of standardizing this viscometer so as to convert the times of efflux into absolute viscosity values, see p. 156.

Saybolt's Viscometer.—*Construction.*—This instrument, fig. 40, is constructed entirely of metal, and in common with many viscometers the amount of oil which runs out during the experiment is measured in a separate vessel. The efflux-tube consists of a wide cylindrical upper portion, A, surrounded at the top by a fixed gallery, B, into which the superfluous oil overflows and from which it is withdrawn by a pipette. The tube A terminates at the

lower end in a metal jet. The jet of an instrument kindly lent to the authors by Mr. Colin Strong of the Anglo-American Oil Co. measured about 17 mm. in length and about 1·6 mm. in internal diameter. The temperature of the liquid, usually water, in the outer bath, C, is raised, when necessary, by means of a ring burner, D. No stirrer is provided, neither is there any means of running off the liquid from the bath C. The oil flowing from the jet is received in a measuring flask, F, which has a mark on the neck at 60 c.c.
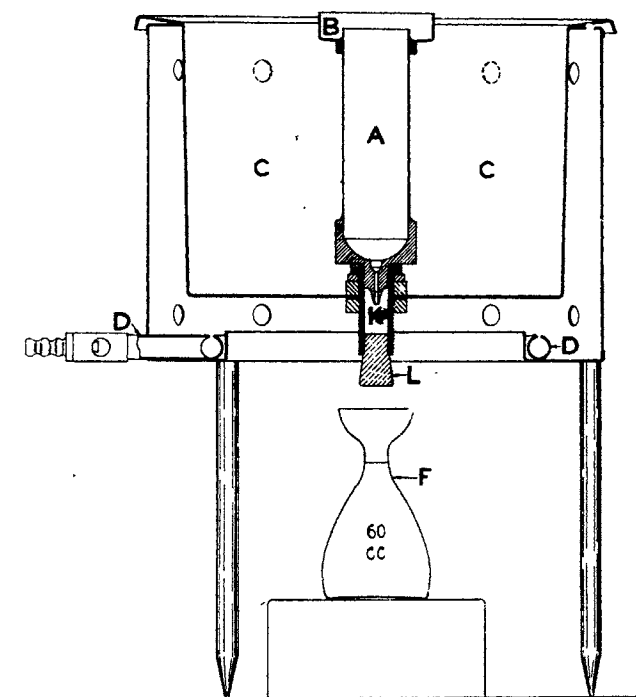
Fig. 40.—Saybolt's Viscometer. (Section of Pipette.)

Method of Experiment.—The outer bath is filled with a suitable liquid, and the temperature is adjusted by the addition of cold liquid or by heating, as may be necessary. The tube K, which encloses the jet, is closed by a cork, L, which is inserted just far enough to be air-tight, and not nearly far enough to touch the jet. The oil, previously strained into a tin cup and heated to about the required temperature, is poured into the tube A until it overflows and fills B above the level of the upper end of A ; it is then stirred with a thermometer until the temperature is exactly adjusted. The thermometer is withdrawn, and the surplus oil is removed from the

gallery B by a pipette. The cork, L, is then withdrawn, and the time occupied in filling the flask to the 60 c.c. mark is noted by a stop-watch and recorded as the viscosity.

In the instrument lent to the authors the time required for 60 c.c. of water at 70° F. to run out was 29 5 seconds ; 50 c.c. of water from Redwood's instrument, at the same temperature, required 25·7 secs.

Engler's Standard Viscometer.—*Construction.*—This instrument is shown in fig. 41. The inner oil vessel, A, is made of brass, gilt inside, and has a lid A¹, which carries the thermometer t. In the centre of the concave bottom is the jet a, 20 mm. long, 2·9 mm. in diameter at the upper end, tapering to 2·8 mm at the lower end ; it is made of platinum for standard work, but for ordinary work brass is used. The plug valve b, of hard wood, which closes the jet, passes through a tube fixed in the lid, and can be raised without removing the cover. Three pointed studs, C, fixed at equal distances above the bottom of the vessel, indicate the proper height of the oil, and at the same time serve for levelling the instrument ; they mark a volume of 240 c.c. The outer bath, B, is filled with water when working at temperatures not exceeding 50° C. ; above that temperature, a heavy mineral oil is used, which can be heated by means of the ring burner d. The oil flowing from the jet is received in the measuring flask, C, which has a mark at 200 c.c. and another at 240 c.c.

FIG. 41.—Engler's Standard Viscometer.

Method of Standardizing.—This is done with water at 20° C. The vessel A is first thoroughly rinsed out successively with ether, alcohol, and water, the jet being cleaned by means of a feather or a roll of paper. After the water has drained out, the jet is closed by the valve. The measuring flask is filled to the 240 c.c. mark with water at 20° C., which is then poured into the oil cup A, and should fill it exactly to the level of the studs after the flask has been well drained. The outer bath should be previously filled with water at 20° C. Having adjusted the surface level, if necessary, by taking out or adding a few drops of water, the temperature of the water both inside and outside the cup is brought exactly to 20° C. and then, after allowing time for the water in A to become perfectly still, the plug valve is raised and the water allowed to flow from A into the dry measuring flask. The time of efflux will be from 50 to 53 seconds, if the instrument has been made of the standard dimensions given in the figure. The test must be repeated, and the mean of three experiments which do not differ by more than 0·5 second is the efflux time of water at 20° C. The nearest whole number is taken as the unit.

Method of Experiment.—In testing oils, the vessel A and the jet are first thoroughly rinsed with alcohol, then with ether, and dried. The oil, previously strained or filtered to remove suspended matter and water, is poured into A up to the level of the studs, and is stirred by the thermometer until the desired temperature has been reached. The liquid in B is adjusted to the same temperature. After allowing the oil in A to become perfectly still,
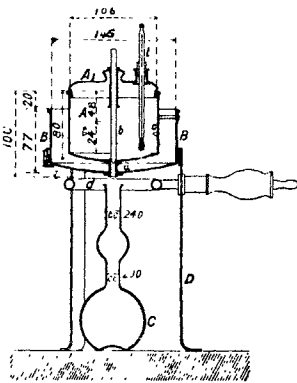
the plug is raised, and the time required for the outflow of 200 c.c. of oil is noted. Supposing the efflux time of water at 20° has been found to be 54 seconds, and the sample of oil required 360 seconds at 50° and 90 seconds at 150°, then the

$$\text{Specific viscosity } (\textit{Engler}) \text{ at } 50° \text{ C.} = \frac{360}{54} = 6\cdot66,$$

$$,, \qquad ,, \qquad ,, \quad \text{at } 150° \text{ C.} = \frac{90}{54} = 1\cdot66.$$

What Engler calls the 'specific viscosity' is, of course, a purely arbitrary number, obtainable by his instrument alone, and only by such of these as are constructed of the proper dimensions. Instruments recognized by Engler as reliable may be obtained from C. Desaga of Heidelberg, and bear the official mark of the Karlsruhe Chemisch-Technische Versuchsanstalt or the Charlottenburg Technische Anstalt. Engler's viscometer has been adopted by the Committee of the German State Railways.

Holde[1] finds that in testing thick oils time may be saved by collecting 50 c.c. or 100 c.c. instead of 200 c.c., the results when multiplied by 5 or 2·35, respectively, being concordant with those obtained in the ordinary way. He also suggests that the oil-bath should be covered, and a reflux condenser attached so as to condense and return the vapour; liquids of fixed boiling-point, such as aniline (184° C.) and naphthalene (217° C.), might then be used for high temperature experiments.

The Engler-Kunkler Viscometer.—*Construction.*— Engler's viscometer has the defect of containing no stirrer, and, when making tests at high temperatures, it is found that the temperature of the oil varies sensibly during efflux. Engler and Kunkler have accordingly designed a modified instrument in which the viscometer and measuring flask are enclosed in a double-walled octagonal air-bath made of stout brass plate, 35 cm. high and 20 cm. wide, figs. 43 and 44. It stands upon four triangular feet, *a*, the outer sloping sides of which rest on the inside edge of the ring of a tripod-stand, so that, by shifting the apparatus about, the oil in the cup can be easily levelled. The oven is heated by the flame of a Bunsen burner placed under the copper bottom plate, *b*, which has a deep concavity in the centre and is screwed to the bottom flange with an asbestos ring between. Supported above this on the stand *c*, and shielded from direct radiation by the double asbestos disc *f*, is the measuring flask *e*. The viscometer stands upon four legs on the plate *g*, which rests upon a projecting rim; this plate has a hole in the centre for the oil to pass through, and four oval tubes, *i*, reaching above the rim of the oil-vessel, through which and the central hole the heated air from below circulates and maintains a uniform temperature. Glass windows *ll* and *mm* in opposite sides of the casing, and another in the lid, illuminate the interior and enable the necessary observations to be made. Passing through the centre of the cover there is a stirring apparatus, consisting of a tubular axis carrying three blades at the lower end, and furnished with a knob at the upper end by which it is rotated to and fro; stops on the lid prevent it revolving more than one-third of a turn, and also prevent the blades from coming into contact with the bulb of the thermometer *s*. The plug-valve, *t*, passes through the axis of the stirrer, which can be lifted out of the oil and suspended by a projecting stud before the valve is raised. The stirrer is made in two parts, which can be easily separated for cleaning. The oil is poured into the cup through the tube *v*, having previously been

heated to the required temperature in the double-walled can, fig. 42, which is also provided with thermometer and stirrer.

Method of Experiment.—The flask is first placed upon the stand *c* ; then the plate *g* and viscometer are put in their places and the cover is firmly fixed on, taking care that the marks on the plate, viscometer, and cover are opposite to the mark on the side of the oven. The outer thermometer, *u,* is placed with its bulb next to the viscometer, and the thermometer *s,* which registers the temperature of the oil, is pushed down until its bulb nearly reaches to the bottom of the cup. The tube *v* is inserted, the stirrer is lowered into the viscometer, and the jet is closed by means of the valve *t*. Having levelled the apparatus by means of the plumb-line at the side, heat
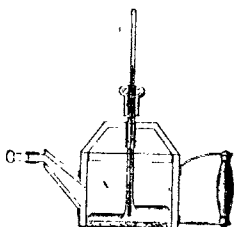
FIG. 42.
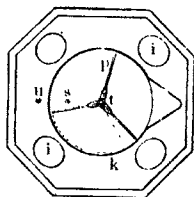
FIG. 43.
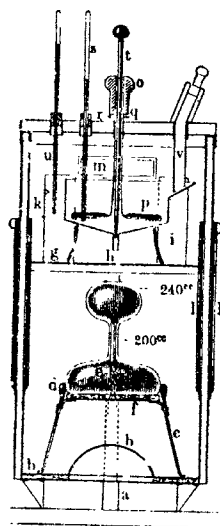
FIG. 44.

is at first applied strongly, until about four-fifths of the desired rise of temperature has taken place, and then the flame is gradually lowered until the temperature is reached and remains constant. The outer thermometer, *u,* must alone be observed at this stage, as a layer of somewhat cooler air lies at the bottom of the oil-cup. Meanwhile, the can *x,* having been filled with oil nearly up to the mark, is heated to the required temperature whilst the stirrer is rotated in the direction of the arrow-mark on the lid, and then the surface of the oil is adjusted to the mark exactly. When the temperature of the air in the oven is constant, and that of the oil in the can is from 0·25° to 0·5° higher, the oil is quickly poured down the tube *v,* the can being well drained, and the tube is then stoppered. Having made certain that the surface of the oil is level with all the studs on the viscometer, the stirrer is worked whilst the valve-rod is held firmly in position, and the temperature of the oil is finally adjusted. The stirrer is then lifted out of the oil and suspended by its stud, the valve rod is withdrawn, the hole being closed with

a cork, and the number of seconds required to fill the flask up to the 200 c.c. mark is exactly noted.

Method of Standardizing—This instrument is standardized in the same manner as the Engler viscometer.

Doolittle's Torsion Viscometer.[1]—This instrument, which is much used in American laboratories, was devised by O. S. Doolittle for use in the laboratory of the Pennsylvania and Reading Railroad Company. It has been in constant use there for over eleven years, and has given very satisfactory results.

The apparatus (fig. 45) consists of a steel wire, suspended from a firm support, and fastened to a stem which passes through a graduated horizontal disc, by means of which the torsion of the wire may be measured. The disc is adjusted so that the index points to zero when there is no torsion in the wire. A cylinder, 2 inches long by 1½ inches in diameter, having a slender stem by which to suspend it, is then immersed in the oil to be tested and fastened by a thumb-screw. The oil is surrounded by a bath of water or paraffin, according to the temperature at which the experiment is to be made. The temperature being adjusted whilst the disc rests upon its supports, the wire is twisted 360° by means of the knob at the top. The disc being released, the cylinder rotates in the oil, owing to the torsion of the wire. If there were no resistance to the movement, the momentum acquired by the cylinder and disc in revolving back to zero would carry them to 360° in the opposite direction; but the resistance of the oil causes the revolution to fall short of 360°, and this resistance is stated to be directly proportional to the viscosity of the oil.

Fig. 45.—Doolittle's Torsion Viscometer.

The simplest way in which the resistance may be measured is by observing the number of degrees of retardation between the first and second complete arcs traversed by the disc. Supposing, for example, that the wire be twisted 360° and the disc released. The first reading is taken at the end of the first swing; say 355·6° to the right. The disc is allowed to swing back to the left and no reading is taken, but the second reading is made at the end of the next swing to the right; say 338·2°. We thus have :—

Right,	355·6°
Left,	
Right,	338·2°
Retardation,	17·4°

[1] *Jour. Amer. Chem. Soc.,* xv. (1893), 173, 454; Allen, *Comml. Org. Anal.,* vol. ii. part ii p. 125.

To avoid error, two tests are made, one by rotating the milled head to the left and the other to the right. If the instrument be in correct adjustment, the two results will be the same ; but if it be slightly out of adjustment, the mean of the two will be the correct reading.

In order to overcome the variations in different instruments, each is standardized against pure cane-sugar solutions, and the viscosities of oils are expressed in terms of the number of grammes of pure cane sugar which, contained in 100 c.c. of the syrup at 60° F., will at 80° F. give the same retardation as the oil. Readings are obtained by making a number of solutions containing known amounts of pure cane sugar, and determining the retardation of each. A curve is then marked out on squared paper, the number of grammes of sugar in 100 c.c. of the different syrups being taken as abscissæ and the degrees of retardation as ordinates. From this curve the value of each degree of retardation in terms of cane sugar is interpolated, and the values, arranged in the form of a table, are furnished with each instrument.

One advantage of the torsion viscometer is that the observations are quite independent of the specific gravity of the liquid. Observations at high temperatures can be readily made, and a moderate amount of suspended matter in the oil does not affect the readings. It might be supposed that inertia effects would vitiate the results and become proportionally greater the less viscous the oil. In regard to this, R. Job writes : [1] "We have spent a good deal of time in experimenting on the matter, and have found that the error due to this source is hardly measurable, owing to the fact that the wire is over 20 inches long and the cylinder head weighs over five pounds, while the cylinder itself is only 2 inches high and 1½ inches in diameter. Thus, we have comparatively slow movement with considerable momentum, so that the reading is practically unaffected by the slight movement of the solution." Job also states that after allowing the weight to remain suspended for a short time, no further stretching of the wire takes place.

The Expression of Viscosity Values.

Although viscosity is a definite physical property of liquids, which can be accurately ascertained experimentally and expressed in absolute measure, it has been the custom commercially, ever since the introduction of mineral lubricating oils, to select either rape, olive, or some other fixed oil as a standard and to compare the fluidities of mineral oils with it. From a practical point of view this method is recommended by its simplicity, and provided the viscosities of the oils which is desired to compare do not fall below a certain limit, which in the use of Redwood's viscometer is about the viscosity of sperm oil at 0° F., the relative efflux times of the oils are very nearly proportional to their relative fluidities. It has, however, been objected that owing to the natural variation in viscosity of different samples of the same kind of oil, even when pure, and the much greater differences which may be caused by the use of an adulterated sample as a standard, a fixed oil is not a suitable standard to employ. To meet this objection, Redwood has designed his standard viscometer, the principal dimensions of which are fixed, and each instrument adjusted so as to deliver average rape oil at the same velocity. Engler's viscometer, used in Germany, is also of fixed dimensions, and there

[1] Private communication.

water is the standard of comparison; but the so-called 'specific viscosities,' obtained by dividing the times of efflux of oils with that of water, are purely arbitrary numbers, and the same is true of Kunkler's viscosity-numbers, which are referred to a standard mixture of glycerol and water of low viscosity, and of Doolittle's viscosity values, which are referred to cane sugar solutions of known strength. Such arbitrary numbers may, nevertheless, be sufficient for specification purposes, provided the means of measuring them accurately, and with the certainty of common agreement, exists.

Notwithstanding the efforts which have been made to bring about uniformity in the measurement and expression of viscosity values, much difference of practice still prevails. Numbers of viscometers are in use differing from each other in pattern and dimensions, and yielding results which have no meaning to anyone except the possessor of the particular instrument. Results are frequently expressed in seconds, without any information as to the exact significance of the numbers. Thus, although a knowledge of the viscosity of a lubricating oil is one of the most important factors in judging of its suitability for a particular purpose, no generally intelligible method hitherto proposed of expressing the viscosity has met with more than a limited acceptance. The universal adoption of any particular standard instrument giving arbitrary numbers is probably too much to expect. What is wanted is a system of standardizing, which will enable the viscosity of an oil in absolute measure to be deduced from the time of efflux measured in the ordinary way in any well-designed commercial viscometer. Such a system of standardizing we proceed to explain.

The Standardizing of Commercial Efflux Viscometers.

Mixtures of glycerol and water are prepared ranging in viscosity from about 0·05 to about 5·0, a suitable series for the Redwood viscometer being the following :—

TABLE XXXI.

Mixture No.	Glycerol per cent.	Specific Gravity at $\frac{20°}{20°}$ C	Approximate Viscosity at 20° C.
1	44·4	1·1129	0·046
2	57·0	1·1469	0·086
3	66·0	1·1712	0·157
4	70·6	1·1836	0·228
5	75·3	1·1963	0·350
6	80·4	1·2101	0·596
7	90·8	1·2381	2·39
8	94·8	1·2485	4·73

Mixtures approximating as nearly as possible to these are prepared by weighing and mixing together the required proportions of the purest commercial glycerin and water. The specific gravity of each

fluid at $\frac{20°}{20°}$ C. is then carefully determined as directed on p. 174, and each fluid is run from the viscometer in succession at 20° C.,[1] the experiments being made in duplicate and the mean time taken. Care must be taken to prevent the absorption of water by the stronger glycerins. Finally, pure water is run from the viscometer at 20° C. Of each fluid we now know—

1. The *viscosity* (η), in dynes per sq. cm. at 20° C., which is ascertained from the table on pp. 140-143.
2. The *time* (t), in seconds, required for the outflow of the standard volume (50 c.c. in the case of Redwood's viscometer) at 20° C.
3. The *density* (d), which is calculated by multiplying the sp. gr. at $\frac{20°}{20°}$ C. by 0·998259, the density of water at 20° C.

If the viscometer were perfect, the corrected time (td) would be proportional to the viscosity ; *i.e.*,

$$ktd = \eta,$$

k being a constant the value of which could be ascertained by running a single fluid of known density and viscosity from the viscometer. But it will be found that the value of k deduced from each of the different fluids (including water) varies, greatly in the case of the thinner fluids, but only slightly with fluids above a certain viscosity, and by plotting the results a curve can be drawn from which the value of k for a fluid of any viscosity can be ascertained. Having constructed such a diagram for any viscometer, a multiplier is obtained by which the 'td' of any oil, *i.e.* the time of efflux × the density at the temperature of efflux, may be converted into the viscosity of the oils in dynes per sq. cm. at the temperature of experiment.

TABLE XXXII.—THE REDWOOD VISCOMETER.

Number and Description of Fluid.	Viscosity at 20° C. η (dynes per sq. cm.).	Time of Efflux at 20° C. t (seconds).	Density of Fluid at 20° C. d.	td.	$\eta \div td$ $= k$.	Variation of k per cent.
1. Water, .	0·01028	26·0	0·99826	25·95	0·00040	− 83·3
2.	0·0377	33·4	1·0989	36·7	0·00103	− 56·9
3.	0·2360	87·2	1·1828	103·1	0·00229	− 4·2
4. Glycerol and water,	0·4984	174·7	1·2036	210·3	0·00237	− 0·8
5.	0·750?	259·5	1·2134	314·9	0·00238	− 0·4
6.	1·1123	383·,	1·2218	468·8	0·00237	− 0·8
7.	2·2674	772·7	1·2351	954·4	0·00238	− 0·4
8.	4·0356	1343·0	1·2440	1670·7	0·00242	+ 1·3
9.	8·8370	2900·0	1·2548	3638·0	0·00243	+ 1·7

[1] The standardizing *must* be done at *exactly* 20° C., because that is the only temperature at which the values in the table of glycerin viscosities are correct.

We give the results obtained by standardizing in this manner two commercial viscometers (really four; since the Coleman-Archbutt viscometer may be regarded as three instruments of different capacities having a common jet). See Tables XXXII. (p. 157) and XXXIII.

TABLE XXXIII.—THE COLEMAN-ARCHBUTT VISCOMETER.

Number and Description of Fluid.	Viscosity at 20° C. η (dynes per sq. cm.).	Time of Efflux at 20° C. t (seconds).	Density of Fluid at 20° C. d	$td.$	$\eta \div td \atop k.$	Variation of k per cent.
			100 c.c.			
1. Water.	0·01028	28·10	0·998259	28·05	·00037	− 81·7
2.	0·0377	36·25	1·0989	39·8	·00095	− 53·0
3.	0·2338	104·6	1·1825	123·7	·00189	− 6·4
4. Glycerol	0·4984	205·9	1·2036	247·8	·00201	− 0·5
5. and	0·7504	303·1	1·2134	367·8	·00201	+ 1·0
6. water.	1·1123	446·7	1·2218	545·2	·00204	+ 1·0
7.	2·2674	913·8	1·2351	1128·6	·00201	− 0·5
8.	4·0356	1604·5	1·2440	1996·0	·00202	± 0·0
			50 c.c.			
2.	0·0377	22·05	1·0989	24·2	·00156	− 49·4
3.	0·2338	67·65	1·1825	80·0	·00292	5·2
4. Glycerol	0·4984	135·15	1·2036	162·7	·00306	− 0·6
5. and	0·7504	197·7	1·2134	239·9	·00313	+ 1·6
6. water.	1·1123	292·85	1·2218	357·8	·00311	+ 1·0
7.	2·2674	601·2	1·2351	742·5	·00305	1·0
8.	4·0356	1056·5	1·2440	1314·3	·00307	− 0·3
			25 c.c.			
2.	0·0377	12·7	1·0989	14·0	·00269	− 46·6
3.	0·2338	41·45	1·1825	49·0	·00477	− 5·4
4.	0·4984	82·95	1·2036	99·8	·00499	− 1·0
5. Glycerol	0·7504	120·4	1·2134	146·1	·00514	+ 2·0
6. and	1·1123	178·4	1·2218	218·0	·00510	+ 1·2
7. water.	2·2674	369·1	1·2351	455·9	·00497	− 1·4
8.	4·0356	648·5	1·2440	806·7	·00500	− 0·8
9.	8·8370	1396·0	1·2548	1751·7	·00504·	± 0·0

From the results in these tables it appears that the mean values of k deduced from the efflux velocities of the fluids of 0·4984 viscosity and upwards might be used to calculate the viscosity in absolute measure of all oils exceeding in value 0·49, or we might say of all oils of not less viscosity than sperm oil at 60° F. ($\eta = 0·4_2$), with a maximum error, in the case of either instrument, of ± 2·0 per cent. To enable the viscometers to be used for fluids of lower viscosity,

such, e.g., as rape oil at 150° F. ($\eta = 0.18$) or cylinder oils at 212° F. ($\eta = 0.16$ to 0.36), the results have been plotted on diagrams. Fig. 46 gives the complete curves for all liquids. Fig. 47 gives, on an enlarged scale, the first part of each curve for thin liquids.[1]

FIG. 46.—Correction Curve for the Coleman-Archbutt and Redwood Viscometers.

Value of k.

Value of td (thick liquids).
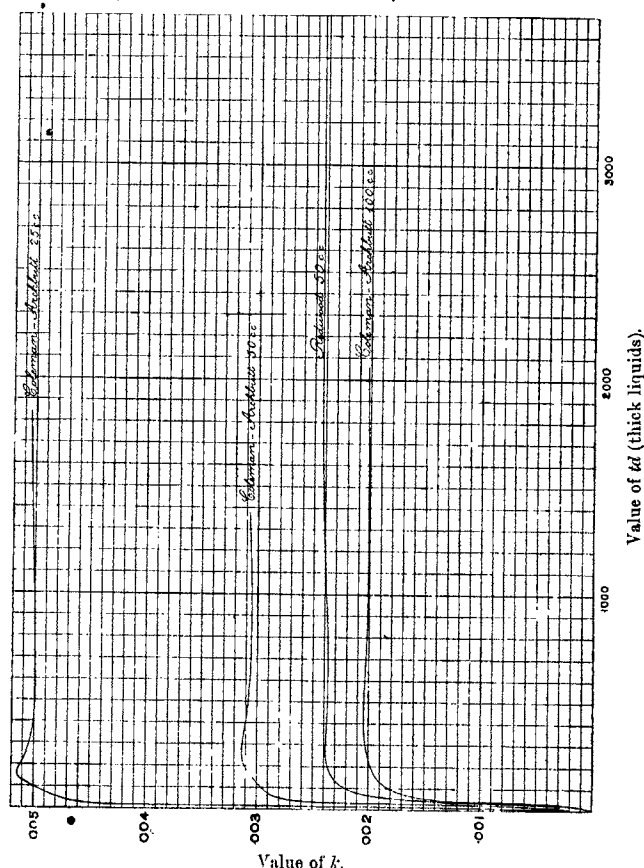
The success of this method of standardizing depends upon the flow of liquid through the jet of the viscometer being free from eddying motion, and provided the length of the jet does not exceed twenty times its diameter steady motion may be relied upon in the case of

[1] These diagrams are, of course, applicable only to the particular instruments for which they were constructed.

liquids of not lower viscosity than 0·4. With thinner liquids unsteady

FIG. 47.—Correction Curve for the Coleman-Archbutt and Redwood Viscometers.

Value of k.
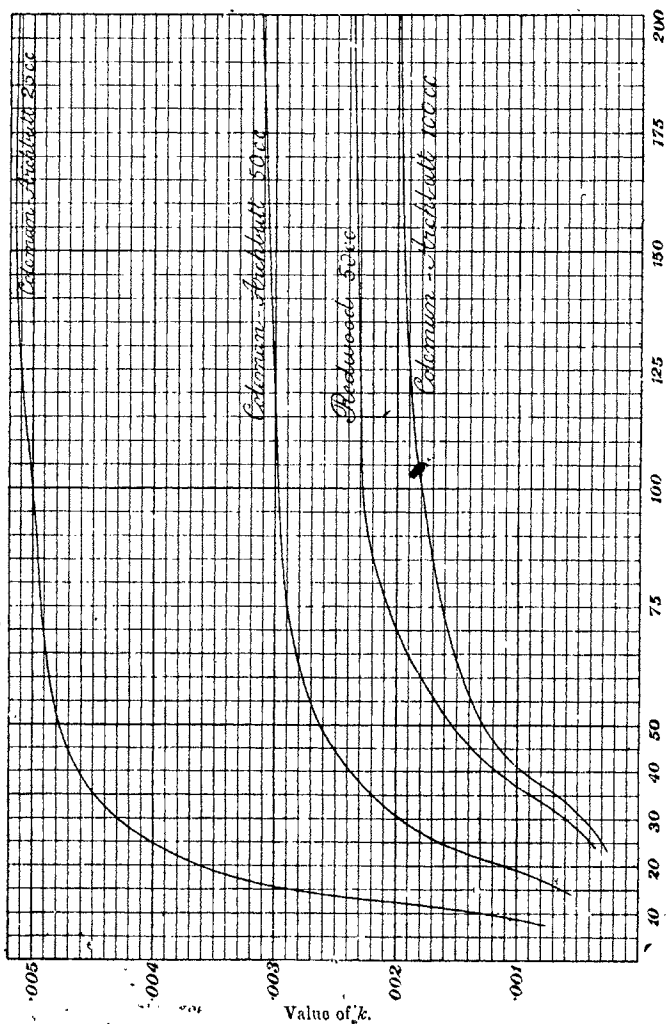
motion may occur, and the tendency to form eddies will be greater, *ceteris paribus*, the higher the density of the liquid and the lower its

viscosity. That is to say, the comparatively heavy glycerol solutions used for standardizing will be more likely to set up eddies than the lighter oils, and consequently the latter may flow more rapidly than glycerol solutions of equal viscosity. With both the viscometers tested by us this has been found to be the case, and the value of k corresponding to the td of thin oils is too small to give the true viscosity. If, however, the value of k corresponding to $1\frac{2}{5}$ td be taken, practically correct results are obtained, even with oils as thin as water. We, therefore, apply this correction to all thin oils. The following rules contain a summary of the method.

RULES FOR DETERMINING BY MEANS OF A STANDARDIZED VISCOMETER THE VISCOSITY OF A LUBRICATING OIL IN ABSOLUTE MEASURE AT ANY DESIRED TEMPERATURE.

A. For Oils of Viscosity 0·4 and upwards.

1st. Determine the time of efflux (t) of the standard volume in seconds.
2nd. Determine the density (d) of the oil at the same temperature.
3rd. Find the value of k corresponding to td.
4th. Multiply td by k; the product is the absolute viscosity.

B. For Oils of Lower Viscosity than 0·4.

1st and 2nd. As above.

3rd. Find the value of k corresponding to $\dfrac{7td}{5}$.

4th. Multiply td by k; the product is the absolute viscosity.

The following results show the accuracy of which the method is capable. Oils of low viscosity were selected for experiment, as with these the error is likely to be greatest.

Description of Oil.	Density at 20° C.	Absolute Viscosity at 20° C., determined by means of the		
		Absolute Viscometer.	Redwood Viscometer.	Coleman Viscometer.
Mixture of shale oil and petroleum, .	0·8265	0·040	0·040	0·042
Shale oil, ...	0·8653	0·124	0·123	0·122
Sperm oil, ...	0·8783	0·377	0·377	0·378

Tables XXXIV. and XXXV. contain the complete results obtained by testing in this manner a number of lubricating oils. Table XXXVI. is a summary. The curves in figs. 48, 49, 50, 51 show the relation between absolute viscosity and temperature in the case of mineral lubricating oils, as compared with typical animal and vegetable oils.

11

'Table XXXIV.—Viscosities of Oils in Dynes per sq. cm. determined by the Coleman-Archbutt Viscometer.

Description of Oil.	60° F.				
	Efflux Velocity (seconds) t.	Density d.	td.	k.	Viscosity $\eta = ktd$.
Animal and Vegetable Oils.	100 c.c.				
Sperm oil,	240·4	·8783	211·1	·00199	0·420
Olive oil,	539·2	·9159	493·9	·00204	1·008
Rape oil,	598·6	·9151	547 8	·00204	1·118
Tallow,	...	...	...	...	...
Castor oil,	...	...	...	...	...
Neutral wool fat,	...	...	...	...	...
Scotch Mineral Oils.					
'865,'	90·7	·8683	78·8	·00185	0·146
'890,'	284·4	·8905	253·3	·00201	0·509
Galician Mineral Oils.					
Light (pale) machinery oil,	215·0	·8785	191·0	·00203	0·388
Heavy (pale) machinery oil,	695·0	·8961	622·8	·00203	1·264
Russian Mineral Oils.					
Light machinery and spindle oil,	631·3	·8972	566·8	·00204	1·156
Medium (pale) machinery oil,	1955·0	·9096	1778·3	·00202	3·592
	50 c.c.				
Heavy(pale) engine and machinery oil,	1838·0	·9085	1669·8	·00310	5·176
Heavy (dark) axle oil,	2152·0	·9092	1956·8	·00310	6·066
Extra heavy (pale) engine and machinery oil,	2186·0	·9085	1986·0	·00310	6·157
American Mineral Oils.	100 c.c.				
Spindle oil ('Pale 885'),	256·2	·8844	226·6	·00200	0·453
,, ,, ('Pale 860/70'),	410·5	·8677	356·2	·00204	0·727
Light machinery oil ('900/7')	619·5	·9008	558·1	·00204	1·138
'Solar red' engine oil,	1040·0	·9162	952·8	·00201	1·915
'Bayonne' engine oil,	1185·6	·9113	1080·5	·00201	2·172
	50 c.c.				
'Special red' engine oil,	1048·0	·9357	980·6	·00306	3·001
Medium (dark) machinery oil,	1130·0	·8839	998·8	·00307	3·046
'Galena' axle oil,	1555·0	·9086	1412·9	·00309	4·366
Heavy (pale) machinery oil,	2363·0	·9018	2131·0	·00310	6·606
Filtered cylinder oil ('Valvoline'),	...	...	...	...	...
,, ,, ,, ('F.F.F.'),	...	...	...	...	...
Dark cylinder oil ('A'),	...	...	...	...	...
,, ,, ,, ('N'),	...	...	...	...	...
,, ,, ,, ('Locomotive'),	...	...	...	...	...
Dark filtered-cylinder oil ('N'),	...	...	...	...	...

TABLE XXXIV.—*continued.*

Description of Oil.	Efflux Velocity (seconds) t.	Density d.	td.	k.	Viscosity η = ktd
Animal and Vegetable Oils.	100 c.c.				
Sperm oil,	111·7	·8637	96·5	·00192	0·185
Olive oil,	208·2	·9011	187·6	·00201	0·377
Rape oil,	235·6	·9005	212·2	·00199	0·422
Tallow, .	...	...	...	...	...
Castor oil,	1433·0	·9473	1357·5	·00201	2·729
Neutral wool fat,	...	...	...	...	...
Scotch Mineral Oils.					
'865,'	52·0	·8533	44·4	·00148	0·066
'890,'	108·9	·8761	95·4	·00192	0·183
Galician Mineral Oils.					
Light (pale) machinery oil,	97·0	·8741	84·8	·00167	0·142
Heavy (pale) machinery oil,	205·0	·8822	180·9	·00189	0·342
Russian Mineral Oils.					
Light machinery and spindle oil,	174·9	·8837	154·6	·00190	0·307
Medium (pale) machinery oil,	417·0	·8357	373·5	·00204	0·762
Heavy (pale) engine and machinery oil,	579·0	·8949	518·1	·00203	1·052
Heavy (dark) axle oil,	673·0	·8955	602·7	·00203	1·223
Extra heavy (pale) engine and machinery oil,	670·0	·8946	599·4	·00203	1·217
American Mineral Oils.	100 c.c.				
Spindle oil ('Pale 885'),	99·2	8700	86·3	·00188	0·162
,, ('Pale 860/70'),	141·0	·8535	120·3	·00196	0·236
Light machinery oil ('900/7'),	193·0	·8867	171·1	·00200	0·342
'Solar red' engine oil,	273·4	·9020	246·6	·00201	0·496
'Bayonne' engine oil,	315·4	·8973	283·0	·00202	0·572
'Special red' engine oil,	324·0	·9217	299·0	00197	0·589
Medium (dark) machinery oil,	397·6	·8695	345·7	·00204	0·705
'Galena' axle oil, . ,	498·0	·8946	445·5	·00204	0·909
Heavy (pale) machinery oil,	711·0	·8878	630·8	·00203	1·274
Filtered cylinder oil ('Valvoline',	50 c.c. 901·0	·8757	788·9	·00305	2·406
Filtered cylinder oil ('F.F.F.'),	25 c.c. 964·0	·8757	844·2	·00500	4·221
Dark cylinder oil ('A'),	955·0	·8846	844·8	·00500	4·224
,, ,, ('N'),	1438·0	·8849	1272·5	·00503	6·401
,, ,, ('Locomotive'),	1645·0	·8834	1453·2	·00504	7·324
Dark filtered cylinder oil ('N')	2219·0	·8950	1986·0	·00505	10·029

TABLE XXXIV.—*continued.*

Description of Oil.	150° F.				
	Efflux Velocity (seconds) *t.*	Density *d*	*td.*	*k.*	Viscosity $\frac{\eta}{-ktd}$
Animal and Vegetable Oils.	100 c c.				
Sperm oil,	62·1	·8455	52·5	·00161	0·085
Olive oil,	93 3	·8826	82·3	·00187	0·154
Rape oil,	105·2	·8822	92·8	·00191	0·177
Tallow,	105·2	·8784	92·4	·00190	0·176
Castor oil,	321·2	·9284	298·2	·00203	0·605
Neutral wool fat,	906·0	·9137	827·8	·00202	1·672
Scotch Mineral Oils.					
'865,'	38·2	·8347	31·9	·00113	0·036
'800,'	54·8	·8581	47·0	·00146	0·069
Galician Mineral Oils.					
Light (pale) machinery oil,	...	...	...	...	...
Heavy (pale) machinery oil,	...	...	...	...	...
Russian Mineral Oils.					
Light machinery and spindle oil,	67·9	·8661	58·8	00168	0·099
Medium (pale) machinery oil,	115·4	·8784	101·4	·00193	0·196
Heavy (pale) engine and machinery oil,	...	..	...	...	...
Heavy (dark) axle oil,	...	...	...	...	..
Extra heavy (pale) engine and machinery oil,	...	...	...	...	...
American Mineral Oils.					
Spindle oil ('Pale 885'),	52·2	·8521	44·5	·00148	0·066
,, ,, ('Pale 860/70'),	63·9	·8358	53·4	·00162	0·086
Light machinery oil ('900/7'),	75·5	·8690	65·6	·00175	0·115
'Solar red' engine oil,	91·9	·8843	81·3	·00185	0·150
'Bayonne' engine oil,	103·5	·8797	91·1	·00190	0·173
'Special red' engine oil,	...	...	0...	...	...
Medium (dark) machinery oil,	127·0	·8514	108·1	·00194	0·210
'Galena' axle oil,	...	...	...	...	...
Heavy (pale) machinery oil,	...	...	...	...	...
Filtered cylinder oil ('Valvoline'),	347·0	·8587	298·0	·00203	0·605
,, ,, ,, ('F.F.F.'),	..	...	...	...	...
Dark cylinder oil ('A'),	471·4	·8666	408·5	·00204	0·833
,, ,, ,, ('N'),	...	...	...	..	...
,, ,, ,, ('Locomotive'),	...	...	...	...	...
Dark filtered cylinder oil ('N'),	...	...	...	...	...

TABLE XXXIV.—*concluded.*

Description of Oil.	212° F.				
	Efflux Velocity (seconds) t.	Density d.	td.	k.	Viscosity $\eta = ktd$.
Animal and Vegetable Oils.	100 c.c.				
Sperm oil, ...	43·4	·8229	35·7	·00128	0·046
Olive oil, ...	53·6	·8596	46·1	·00151	0·070
Rape oil, ...	58·7	·8595	50·5	·00158	0·080
Tallow, ...	58·0	·8557	49·6	·00157	0·078
Castor oil, ...	98·9	·9050	89·5	·00189	0·169
Neutral wool fat, . . .	180·0	·8909	160·4	·00196	0·314
Scotch Mineral Oils.					
'865,'	...	...	...		
'890,'	.	...	.	...	...
Galician Mineral Oils.					
Light (pale) machinery oil, .	...	.	...	..	..
Heavy (pale) machinery oil, .			.	...	
Russian Mineral Oils.					
Light machinery and spindle oil,	41·0	·8442	34·6	·00124	0·043
Medium (pale) machinery oil, .	51·8	·8568	44·4	·00148	0·066
Heavy (pale) engine and machinery oil,	...	...	...	...	...
Heavy (dark) axle oil, . .	...	...	...	...	...
Extra heavy (pale) engine and machinery oil, . . .	...	...	...	..	..
American Mineral Oils.					
Spindle oil ('Pale 885'), . .	36·8	·8298	30·5	·00107	0·033
„ „ ('Pale 860/70'), .	40·8	·8138	33·2	·00119	0·039
Light machinery oil ('900/7 '), .	43·8	·8469	37·1	·00132	0·049
'Solar red' engine oil, . .	47·5	·8624	41·0	·00142	0·058
'Bayonne' engine oil, . .	50·4	·8579	43·2	·00146	0·063
'Special red' engine oil, . .	...	...	...	...	...
Medium (dark) machinery oil, .	59·1	·8291	49·0	·00156	0·076
'Galena' axle oil, . . .	...	...	...	...	...
Heavy (pale) machinery oil, .	...	...	...	...	...
Filtered cylinder oil ('Valvoline')	116·0	·8377	97·2	·00192	0·187
„ „ „ ('F.F.F.'), .	159·0	·8370	133·1	·00191	0·254
Dark cylinder oil ('A'), . .	145·0	·8441	122·4	·00196	0·240
„ „ „ ('N'), .	173·0	·8464	146·3	·00193	0·282
„ „ „ ('Locomotive'), .	202·0	·8439	170·5	·00200	0·341
Dark filtered cylinder oil ('N'), .	208·0	·8555	177·9	·00200	0·356

TABLE XXXV.—Viscosities of Oils in Dynes per sq. cm. deter-
mined by the Redwood Viscometer.

Description of Oil.	60° F.				
	Efflux Velocity (seconds) *t*.	Density *d*.	*td*.	*k*.	Viscosity η $= ktd$.
American Mineral Oils.					
'Globe' oil (dark) . . .	653·0	·8802	574·8	·00237	1·362
Light Machinery oil ('905/10')	689·5	·9054	624·3	·00237	1·479
	100° F.				
American Mineral Oils.					
'Globe' oil (dark) . . .	199·6	·8663	173·0	·00234	0·405
Light Machinery oil ('905/10')	200·2	·8915	178·5	·00235	0·419

TABLE XXXVI.—ABSOLUTE VISCOSITIES OF OILS (SUMMARY).

Description of Oil, etc.	Absolute Viscosity (η) in Dynes per sq. cm.			
	60° F.	100° F.	150° F.	212° F.
Water at 68° F. (20° C.), . . .	0·01028			
Animal and Vegetable Oils.				
Sperm oil, ...	0·420	0·185	0·085	0·046
Olive oil, ...	1·008	0·377	0·154	0·070
Rape oil, ...	1·118	0·422	0·177	0·080
Tallow, ...	...	...	0·176	0·078
Castor oil, ...	...	2·729	0·605	0·169
Neutral wool fat, ...	...	..	1·672	0·314
Scotch Mineral Oils.				
' 865,'	0·146	0·066	0·036	...
' 890,'	0·509	0·183	0·069	...
Galician Mineral Oils.				
Light (pale) machinery oil, . .	0·388	0·142	...	...
Heavy (pale) machinery oil, . .	1·264	0·342	..	...
Russian Mineral Oils.				
Light machinery and spindle oil, .	1·156	0·307	0·099	0·043
Medium (pale) machinery oil, . .	3 592	0·762	0·196	0·066
Heavy (pale) engine and machinery oil,	5·176	1·052	...	...
Heavy (dark) axle oil, . . .	6·066	1·223	...	..
Extra heavy (pale) engine and machinery oil, . . .	6·157	1·217	...	...
American Mineral Oils.				
Spindle oil (' Pale 885 '), . .	0·453	0·162	0·066	0·033
„ „ (' Pale 860/70 '), .	0·727	0·236	0·086	0·039
Light machinery oil (' 900/7 '), .	1·138	0·342	0·115	0·049
' Globe' oil (dark), . . .	1·362	0·405	...	...
Light machinery oil (' 905/10 '), .	1·479	0·419	...	...
' Solar red ' engine oil, . .	1·915	0·496	0·150	0·058
' Bayonne ' engine oil, . .	2·172	0·572	0·173	0·063
' Special red ' engine oil, . .	3 001	0·589	...	...
Medium (dark) machinery oil, .	3·046	0·705	0·210	0·076
' Galena' axle oil, ...	4·366	0·909	...	...
Heavy (pale) machinery oil, . .	6·606	1·274	...	...
Filtered cylinder oil (' Valvoline ') .	...	2·406	0·605	0·187
„ „ (' F.F.F.'), .	...	4·221		0·254
Dark cylinder oil (' A '), . .	...	4·224	0·833	0·240
„ „ (' N '), . .	...	6·401	...	0·282
„ „ (' Locomotive ') .	...	7·324	...	0·341
Dark filtered cylinder oil (' N ') .	...	10·029	...	0·356

FIG. 48.—Spindle Oils.

1. Sperm Oil

2 Pale American Oil "885"

3. American Spindle Oil "860/70"

4 Scotch Shale Oil "890"

Absolute Viscosity.

Temperature ° F.

FIG. 49.—Light Machinery Oils.

1.Olive Oil

2.Pale American Oil 900/7

3.Pale Russian Oil 895/900

Absolute Viscosity.

Temperature ° F.
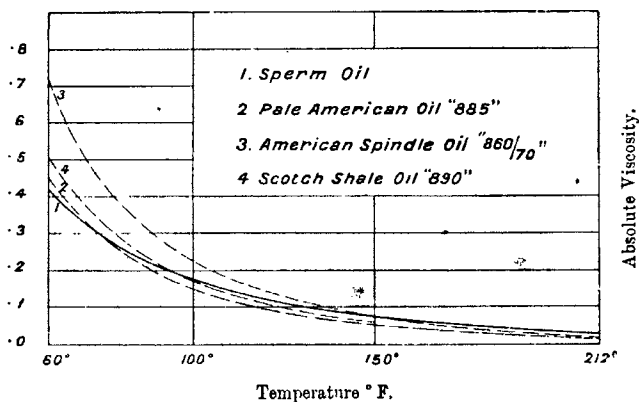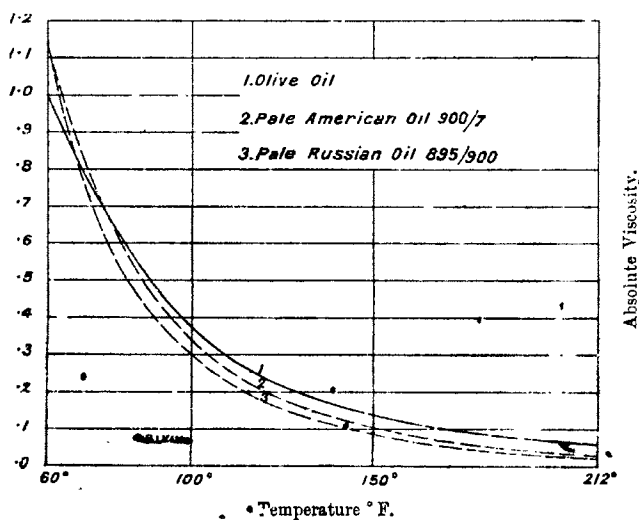
FIG. 50.—Heavy Machinery Oils.

1. Rape Oil
2. American Solar "Red" Engine Oil
3. American "Bayonne" Engine Oil
4. American Dark Med.ᵐ Mach.ˡ Oil
5. Pale Russian Oil 905/7

Absolute Viscosity.

Temperature ° F.

FIG. 51.—Cylinder Oils.

1. Castor Oil
2. American Dark "N" Cylin Oil
3. do: do. "A" do:
4. do: Valvoline do.

Absolute Viscosity.

Temperature ° F.
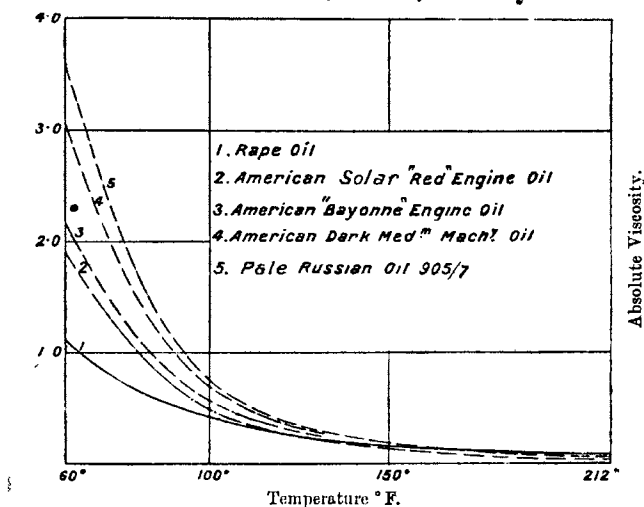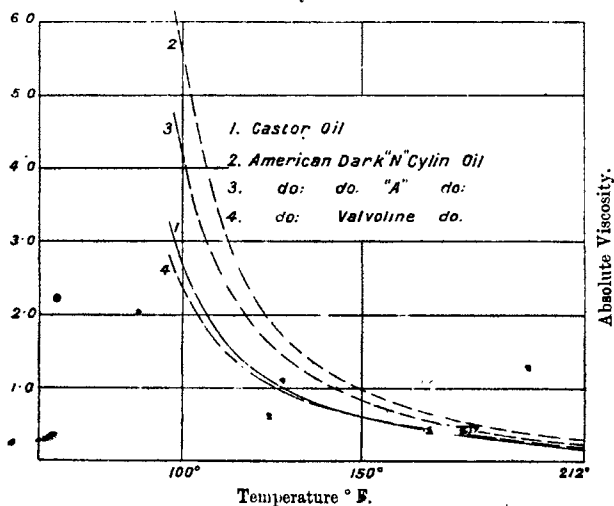
Apparatus for Determining the Consistence of Solid Fats and Greases.

Kissling's Apparatus, shown in fig. 52, is constructed and used as follows :—
A rod, 30 c.m. long and 8 to 10 mm. in diameter, passes loosely through a
hole in the plate *f.* The lower end of the rod is pointed, and to the upper
end is fixed a weight P. The fat or grease is contained
in a beaker, 8 cm. wide and 10 cm. high, which is
placed in such a position that when the point of the
rod rests upon the surface of the fat, the point of the
stud S is exactly 10 cm. above the plate *f.* The rod
is then allowed to sink into the fat, and the time
which elapses before the stud touches the plate is
measured. The number of seconds expresses the rela-
tive consistence of the fat. All experiments with this
apparatus are made at 20° C.
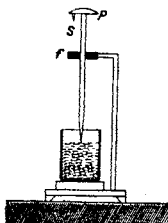
According to the consistence of the fat, either a
brass rod of 150 grammes total weight, or a zinc rod

Fig. 52.—Kissling's   of 100 grammes weight, or a glass rod of 50 grammes
Apparatus for   weight, is used, and the fat must have remained
Greases.   undisturbed for twenty-four hours before the test is
made. If a sufficiently large quantity of the fat is
available, the container may be a thin brass cylinder with a loose bottom,
which is filled by pressing it down into the fat; in this way the fat is not
subjected to mechanical disturbance in filling the vessel. If the repeated
testing of the same fat does not give concordant results, the fact must be
attributed less to a defect in the apparatus than to the sensitiveness of fats
to mechanical disturbance and change of temperature, and to the fact that
their consistence is not always uniform in different parts (*Kunkler*).

Kunkler's Apparatus is shown in fig. 53. It is made of sheet brass, and
the temperature of testing is 50° C. In the water bath *a,* the temperature
of which is maintained by applying heat to the vessel *g,* and registered by
means of the thermometer *f,* the vertical tube *b* is fixed, terminating in the
jet *d,* 6 mm. wide and 15 mm. long. The tube *c,* 30 mm. wide and 150 mm.
long, which contains the fat or grease, slides within the tube *b,* and the
grease is forced out of this tube, through the jet *d,* by means of the piston *e,*
75 mm. in length, consisting of two discs, 29 mm. in diameter, and a
connecting piece.

The tube *o,* forming an upward continuation of the piston, is kept in
position by a projecting strip which slides in the groove *n,* on the inside of
the tube *c.* A cap *h,* the movement of which is restricted by the pin *t*
working in the slot *m,* fits over the upper end of the tube *c,* and acts as a
stop for the brackets *k* and *l,* by which the movement of the piston is arrested
The brackets *k,* which rest upon the cap before the experiment is commenced
are set free by turning the cap to the right ; the piston then commences to
descend, and continues to fall until the second pair of brackets, *l,* rests upon
the cap, when the experiment is at an end and the time is noted. The
distance between the two pairs of brackets is 55 mm. The piston is loaded
with the whole or a portion of the lead weights *r,* three of 200 grammes, one
of 100 grammes, and one of 50 grammes, according to the consistence of the
grease. The weights are kept in position by the rod and disc *p.* The weight
of the piston and rod is 170 grammes.

In using this apparatus, the tube *c* is filled with the grease to be tested

by first inserting the piston e and spreading the grease with a broad knife upon the disc b, and, whilst spreading more and more grease gradually withdrawing the piston until the upper disc reaches the open end of the tube.
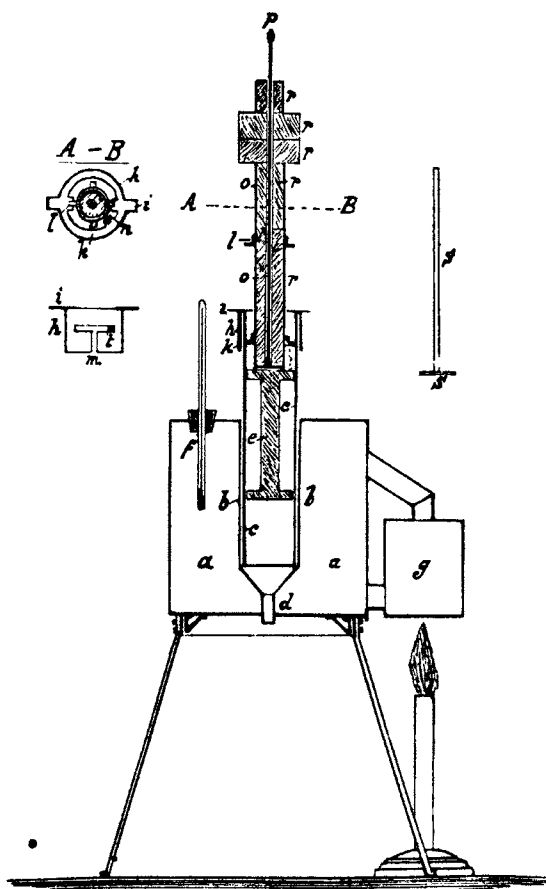
Fig. 53.

Great care must be taken that no air-bubbles are included. After pressing down the grease with the rod and disc s, the piston may be withdrawn and another tube filled, as, owing to the extent to which the consistency of grease is affected by working it about, the tube after filling must remain for at least twenty-four hours at a temperature of about 20° C. before the test is made.

The water-bath is then filled nearly full of water at 55° C., and this temperature is maintained constant during the test. The tube of grease having been inserted into the fixed tube b, the piston is put in and pressed down until the stop, k, rests upon the cap. After the lapse of twenty minutes, the suitably loaded piston is liberated by turning the cap, and the time which elapses before its movement is arrested by the stops, l, measures the consistency of the grease.

This apparatus is intended for comparing the consistency of one sample of grease with another, or of several samples with a standard, and the load put upon the piston must depend upon the consistency of the grease. It should be so proportioned that the time of experiment with the stiffest sample is about ten minutes. It is obvious that the load must be the same for all samples compared, as the results of tests made with different loads do not admit of comparison.

B.—SPECIFIC GRAVITY AND DENSITY.

The specific gravity of a solid or liquid substance is the weight compared with that of an equal volume of water taken as unity. Unless otherwise stated, the comparison is made with water at the same temperature as the substance, but such an expression as 'sp. gr. at $\frac{20°}{4°}$,' means the weight of the substance at 20° compared with water at 4° taken as unity. In the C.G.S. system of units, the specific gravity at $\frac{20°}{4°}$ C. is identical with the *density* of the substance at 20° C.[1]

The specific gravities of the vegetable and animal oils and fluid waxes at 60° F. (15·5° C.) range from about 0·879 in the case of sperm oil, to about 0·968 in that of castor oil, and although individual specimens of each description of oil are liable to vary somewhat in specific gravity, the limits of variation for each of the principal kinds of oil are not wide and are pretty well known. Hence, a knowledge of the specific gravity of an animal or vegetable oil is valuable, both as a means of identification and also in judging of the purity of a particular specimen.

Mineral lubricating oils may also be classified according to their specific gravities (see p. 185), though this property is of secondary importance in relation to their lubricating value. It is, however, of great importance in distinguishing between mineral oils, on the one hand, and rosin and coal-tar oils on the other.

Determination of Specific Gravity.—Practically three methods are in use for determining the specific gravity of liquids, viz. : —1. *By pyknometers.* 2. *By the specific gravity balance.* 3. *By hydrometers.* The first method is applicable to all liquids, however viscous, and is, therefore, the most suitable for lubricating oils. The two last methods are adapted only for liquids of very moderate viscosity, and their applicability to lubricating oils is, therefore, limited.

[1] See Tait, *Properties of Matter*, third edition, p. 30.

The term 'pyknometer' includes any vessel in which an accurately measured volume of a liquid can be weighed ; the kinds in common use are the various forms of specific gravity bottle and the Sprengel tube. Of the former, the plain form, with an accurately ground, finely perforated stopper, is most useful for determining the specific gravities of lubricating oils at ordinary temperatures ; for higher temperatures, and for limited quantities of material, the Sprengel tube is more convenient and accurate.

Bottle Method.—The specific gravity bottle with perforated stopper is shown in fig. 54. It can be obtained of various sizes, but the most suitable for our purpose holds, nominally, 25 grammes of water at 60° F. The capacity marked on the bottle must not be accepted without verification, but the bottle must be calibrated by ascertaining its weight, when empty, and when filled with recently boiled distilled water at 60° F.

To calibrate the bottle.—The bottle before being weighed must first be thoroughly cleaned, rinsed with water, alcohol, and ether in succession, then warmed, and dried by aspirating a current of air to displace the ether vapour. The bottle should not be strongly heated. The stopper, also cleaned and dried, is inserted ; the bottle is allowed to stand in a cool place for ten or fifteen minutes, then wiped with a clean soft rag and

25 Grammes 60°F

Fig. 54.

immediately weighed. Some pure distilled water is next boiled vigorously for about five minutes in a platinum or silver vessel, rapidly cooled to 60° F., and carefully poured into the bottle, avoiding the introduction of air bubbles. The bottle is immediately immersed up to the neck in a capacious basin of water at exactly 60° F., and is allowed to stand at this temperature for a few minutes, the water in the basin being frequently stirred with the thermometer and maintained constant in temperature. The stopper is then inserted in the bottle, well bedded into its seat, and the surplus water which has exuded through the perforation wiped off. If, now, the temperature of the water is the same inside and outside the bottle, the capillary in the stopper will remain exactly full, and there will be neither contraction nor exudation of water. When this is the case, the bottle is lifted out of the water in the basin, and slowly immersed [1] in water several degrees colder, which will cause the water in the bottle to contract and empty the capillary ; the outside of the bottle can now be wiped quite dry and weighed before the water has time to expand and exude from the stopper. Duplicate weighings, if carefully made in the manner directed, will not differ by more than two or three tenths of a milligramme. At least two weighings should be made. The bottle is then dried and again weighed empty. The weight should not differ from the previous weight of the empty bottle by more than 0·5 milligramme. The difference between the mean weight of the bottle when full and empty is the *water capacity of the bottle at 60° F.* This seldom needs to be redetermined ; but the empty bottle should be frequently reweighed, as it may become scratched or chipped in use.

To determine the specific gravity of oil at 60° F.—About 50 c.c. of the oil are poured into a small lipped beaker, stirred with a thermometer, most carefully avoiding the introduction of air bubbles, and brought to exactly 60° F. by immersing the beaker in water 2 or 3 degrees above or below that temperature. The bottle is then filled quite full of the oil, without intro-

[1] Rapid immersion, by causing the bottle to contract first, expels some liquid from the stopper.

ducing any air bubbles, immersed up to the neck in water at 60° F., the
stopper loosely inserted, causing the excess of oil to overflow into the basin,
and then, after waiting about five minutes, bedded firmly into its place,
the excess of oil being wiped off the top of the stopper. Having ascertained
that the temperature is correct, and that the oil is neither expanding nor
contracting, the bottle is cooled, wiped clean and dry, and weighed, exactly
as in calibrating the bottle with water. By subtracting from the total
weight the tare of the empty bottle, and then dividing the difference by the
water capacity of the bottle, the specific gravity of the oil at 60° F. is
obtained. The thermometer used must be verified by comparison with a
standard instrument.

Glycerin and very viscous liquids which cannot be poured into the narrow
neck of the bottle may be manipulated as follows:— The jet is cut off a
30 c.c. pipette, making the delivery nozzle the full bore of the tube, and the
dry pipette is filled with the liquid. The nozzle of the pipette having
been wiped outside, is then inserted into the specific gravity bottle nearly to
the bottom, and the liquid is allowed to quietly flow out. In this way, the
bottle may be easily filled without the introduction of a single air bubble.
The bottle, whilst being filled, is held down in water at the required tempera-
ture, and, when full, the stopper is inserted, and the bottle is allowed to stand
in the water at constant temperature until expansion or contraction has
ceased. The excess of fluid is then removed from the stopper, the bottle is
cooled, wiped clean and dry, and weighed.

Sprengel Tube Method.—Sprengel's very useful pyknometer has the form
of an elongated **U**, the arms of which terminate in two
capillary tubes which are bent at right angles in opposite
directions. One of the capillary tubes has a very fine bore
and is drawn down to a point, the other has a wider bore,
about 0·5 mm. in diameter, and is not drawn down.
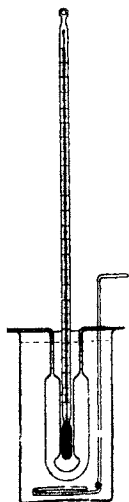
In filling the tube, a small glass bulb, with a piece of
narrow rubber tubing attached to it, is fixed on to the
narrower capillary by means of a perforated rubber stopper,
and the wider capillary is dipped into the oil, which is
then drawn into the tube by suction applied to the rubber
tube, the glass bulb serving as a vacuum chamber. This
is the method described by Sprengel,[1] but with liquids of
moderate viscosity the glass bulb may be dispensed with,
and viscous liquids can usually be reduced in viscosity by
warming, so as to be easily drawn into the tube. When
full, the tube is detached from the bulb and suspended in
a beaker of water, as shown in fig. 55, and the temperature
of the water is maintained constant, with frequent stirring,
until the liquid has ceased to expand or contract. It is
most convenient to arrange the temperature of the liquid
in the tube so that it shall expand, and the liquid is absorbed
by a strip of filter paper until it ceases to exude from the
capillary orifice. The tube is then lifted out of the water
by means of a small brass wire hook, and immersed for a
short time in colder water, so as to contract the liquid and
empty the capillaries. It is then wiped and weighed.

Fig. 55.   The movement of the liquid in expanding or contracting
takes place, as a rule, entirely through the wider capillary,
where there is least resistance. The narrower capillary, when full, generally
remains so, and no liquid is expelled from it unless expansion occurs very

[1] *Jour. Chem. Soc.*, 1873, p 577.

rapidly. If it is necessary to introduce liquid into the pyknometer, owing to contraction having occurred, a drop in the end of a glass tube applied to the point of the narrow capillary will be drawn in.

The water capacity of this pyknometer is determined as in the case of the bottle, and having been done with great care need seldom be redetermined, but the empty tube should be reweighed occasionally.

At 212° *F.* (= 100° *C.*).—For determining the sp. gr. of oils at the boiling-point of water, which for all practical purposes may be assumed to be 212° F., the neck of a 40-oz. flask is cut down as shown in fig. 56, and two opposite nicks are filed in the neck to receive the arms of the Sprengel tube. The flask is filled to the depth of about two inches with hot water, a few fragments of pumice are thrown in, and the water is made to boil vigorously. The filled Sprengel tube is then suspended in the steam, and the open neck of the flask is covered by a watch glass. As soon as oil is no longer expelled from the tube, the ends of the capillary arms are wiped with filter paper and the tube is lifted out of the steam, cooled by immersion in cold water, wiped and weighed. This is the most convenient method of
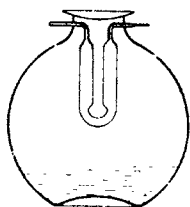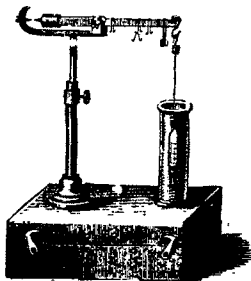
FIG. 56.   FIG. 57.

determining the specific gravities of fatty acids and fats which are solid at the ordinary temperature.

Sprengel tubes may be made to hold as little as 1 c.c., and, with care, the results obtained with a delicate balance are surprisingly accurate. Such small tubes are sometimes useful for determining the specific gravity of the small quantities of fatty acids obtained by saponifying mixed oils in the process of analysis. Sprengel pyknometers are specially adapted for work with hot liquids, as they need not, like bottles, be handled, and their shape causes the temperature of the contained liquid to become quickly adjusted. The movement of the liquid in the delicate capillary tubes indicates the slightest variation of temperature. The only drawback is the tedious nature of the filling and emptying operations with viscous liquids, but this may be largely overcome by warming the liquid so as to reduce the viscosity.

Westphal Balance Method.—The Westphal specific gravity balance (fig. 57) is an instrument of the steelyard type constructed to indicate the specific gravity of a liquid by the relative loss of weight of a plummet of known displacement when suspended in the liquid. The complete instrument consists of the balance proper, the glass thermometer-plummet, the

immersion cylinder, and two exactly similar sets of four rider weights, the largest rider of each set having the same weight as the water which the plummet displaces at 60°. F., the next rider having one-tenth of this weight, the third one-hundredth, and the fourth one-thousandth. The beam is divided by notches into ten exactly equal parts, the notches being points of suspension for the riders and numbered consecutively from 1 to 9.

The balance is set up in a place free from draughts, and is adjusted by means of the levelling screw in the foot, so that when the beam is oscillating with the plummet suspended in air the index finger at the short end of the beam will come to rest exactly opposite to the fixed point. If the plummet be now suspended in water at 60° F., assuming that the instrument is intended for use at that temperature, equilibrium will be exactly restored by suspending one of the largest riders from the same hook as the plummet, indicating a specific gravity of 1·0. But if the liquid be of specific gravity 0·90, equilibrium will be restored by suspending the same rider from notch No. 9 ; if the specific gravity be 0·92, the next largest rider also must be suspended from notch No. 2 ; if the specific gravity be 0·922, the third rider must be hung from the second ; and if the specific gravity be 0·9225, the smallest rider must be hung from notch No. 5. Thus, the specific gravity of any liquid is shown at a glance to four decimal places by the positions of the riders on the beam, the largest rider giving the first decimal place and the other riders the remaining places in order.

Every instrument purchased must, before use, be verified by measuring carefully the distances between the fixed points along the beam, which should not vary more than one-thousandth part. The plummet must also be weighed in air and in water at 60° F., on a good ordinary balance indicating 0·1 milligramme, and the water displaced by the plummet must weigh the same as the largest rider of each set, the other riders varying in decimal proportion. The following table by Stock shows the variations met with in the riders of a Westphal balance by a good maker, the numbers in the third column showing that the maximum deviation from unity did not exceed 1 unit in the fourth decimal place, which is a satisfactory agreement.

TABLE XXXVII.—SHOWING VARIATIONS IN RIDERS.

Rider Number.	Weight in Air. Grammes.	Relation to Unity. Plummet Displacement = 6·48 Grammes.
1	6·4806	1·00007
1a	6·4796	·99992
2	·6482	·10003
2a	·6483	·10004
3	·0655	·01010
3a	·0655	·01010
4	·0070	·00108
4a	·0071	·00109

With a well-made instrument, the probable error of a specific gravity determination will not exceed two or three points in the fourth decimal place with a liquid of low viscosity, such as water or even sperm oil, but the viscosities of most lubricating oils at ordinary temperatures oppose so much resistance

to the movement of the plummet that the probable error becomes much greater. At sufficiently elevated temperatures the viscosities of oils become so much reduced that the Westphal balance may be used for both oils and fats, provided proper allowance be made for the expansion of the plummet. To determine the sp. gr. of a melted fat at $\frac{100°}{100°}$ C., for example, with an instrument constructed for use at some other temperature, we may proceed in the following manner:—First determine by means of the balance the apparent sp. gr. of water at 100° C., $= x$, and then the apparent sp. gr. of the oil at 100° C., $= y$; then $\frac{y}{x}$, with the appropriate correction for vacuo added on (p. 180), is the true sp. gr. of the oil at 100° C. This result × 0·95866 (the density of water at 100° C.) is the density of the oil at $\frac{100°}{4°}$ C.

Fig. 58 shows Carter Bell's method of using the balance for determinations
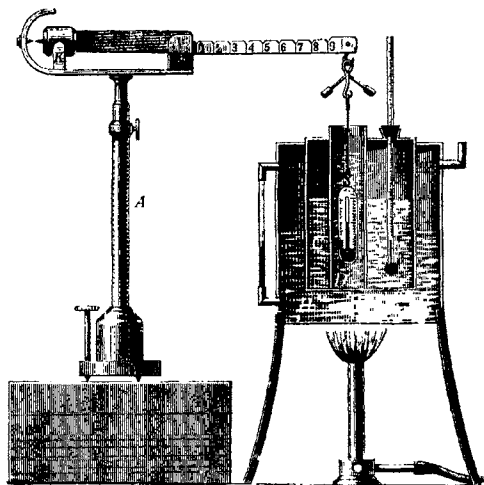
Fig. 58.

at 100° C., D being a glass tube containing the oil or melted fat, C a bath of paraffin wax, and B the water-jacket. The tube for the escape of steam should be prolonged upwards, well above the beam of the balance. A special plummet may be required, as the thermometer of the ordinary plummet has only a limited range.

Hydrometer Method.—Of all methods for ascertaining the specific gravities of liquids this is the most rapid, and provided the instrument used is correctly graduated, or its error exactly known, very accurate results may be obtained by it with liquids of low viscosity. But no hydrometer can be depended upon unless it has been tested by floating it in two or more liquids of which the specific gravities have been determined by means of

12

the pyknometer. From the differences (if any) between the true an
observed values, a table of errors may be constructed for any fairly goo
instrument, by which the readings may be corrected. When the viscosity c
the liquid is great enough to seriously impede the free movement of th
hydrometer, as is the case with most lubricating oils at ordinary tempera
tures, the probable error of the method is greatly increased, and in suc
cases the hydrometer should only be used where speed is of chief importanc
and accuracy a secondary matter.

Hydrometers may be divided into two classes, viz., those giving specifi
gravities directly, and those graduated with arbitrary scales. Hydrometer
of the former class may be purchased of almost any size and range. and al
hydrometers must be used at the temperature for which they have beer
constructed.

A large number of instruments having arbitrary scales are in use. On
of the most common is Lefebre's oleometer. It is intended for use at 15° C
The stem is graduated in degrees, numbered from 1 to 38, and opposit
some of them are the names of certain oils. If immersed in rape oil, i
will sink to the 15th degree, against which the name rape oil appears ; ir
linseed oil it will sink to the 35th degree ; and so on. These numbers
increased by 900, are the specific gravities of the oil compared with wate
$= 1000$. Table XXXVIII. contains a list of hydrometers, the temperature
at which each is intended to be used, and the formula for converting the
degrees into specific gravities.[1]

Alcohol Method.—The foregoing methods are not directly applicable t
solid fats and waxes, but with the aid of a device first suggested by Freseniu
and Schulze, they may be made so. This consists in preparing a mixture o
alcohol and water in which the solid substance neither sinks nor floats, and
taking the specific gravity of the liquid. The same method is obviously
applicable to liquid oils, and is often conveniently employed for ascertaining
the specific gravity of the small quantities of hydrocarbon oil isolated in the
process of analysis.

If a solid substance is being experimented with, it may be prepared for
the test in the manner recommended by Allen and Chattaway. The fat or
wax is melted at the lowest possible temperature and allowed to solidify
spontaneously, without artificial chilling, in a flat-bottomed capsule or watch
glass. Smooth fragments are then cut from it with a knife or cork borer.
In the case of some fats which contract greatly on solidification, such as palm-
nut and coconut oils, it is absolutely essential to allow the substance tc
solidify by standing over night before taking the specific gravity. One of
the fragments thus obtained is held under the surface of dilute alcohol, by
means of forceps, and carefully freed from adhering air-bubbles by means of
a camel-hair brush. The specific gravity of the alcohol is then adjusted
by adding either stronger or weaker alcohol (not water, because of the air-
bubbles formed on mixing) until the fragment remains suspended anywhere
in the liquid. The specific gravity of the diluted alcohol is then determined
by the hydrometer or the Westphal balance. Of course, the final adjustment
of the alcohol must be made exactly at the temperature at which the specific
gravity of the substance is required to be known.

Reduction to the Vacuum.—The apparent weight of a body in air
is less than the true weight by an amount equal to the weight of air
displaced by the body. As this is true of the weights as well as of

[1] See Dittmar; *Chemical Arithmetic*, part i. p. 78 ; also Schaedler, *Technologie der Fette und Oele*, p. 73.

TABLE XXXVIII.—FORMULÆ FOR CONVERTING HYDROMETER DEGREES TO SPECIFIC GRAVITIES.

Hydrometer	Temperature.	For Liquids heavier than Water.	For Liquids lighter than Water.
Balling,	$17 \cdot 5^\circ$ C.	$S = \dfrac{200}{200 - n}$	$S = \dfrac{200}{200 + n}$
Beaumé I.,	$12 \cdot 5^\circ$ C.	$S = \dfrac{145 \cdot 88}{145 \cdot 88 - n}$	$S = \dfrac{145 \cdot 88}{145 \cdot 88 + (n - 10)}$
Beaumé II.,	15° C.	$S = \dfrac{144 \cdot 3}{144 \cdot 3 - n}$	$S = \dfrac{144 \cdot 3}{144 \cdot 3 + (n - 10)}$
Beaumé III.,	$17 \cdot 5^\circ$ C.	$S = \dfrac{146 \cdot 78}{146 \cdot 78 - n}$	$S = \dfrac{146 \cdot 78}{146 \cdot 78 + (n - 10)}$
Beck,	$12 \cdot 5^\circ$ C.	$S = \dfrac{170}{170 - n}$	$S = \dfrac{170}{170 + n}$
Brix,	$\begin{cases} 12 \cdot 5^\circ \text{ R.} \\ 15 \cdot 625^\circ \text{ C.} \end{cases}$	$S = \dfrac{400}{400 - n}$	$S = \dfrac{400}{400 + n}$
Cartier,	$12 \cdot 5^\circ$ C.	$S = \dfrac{136 \cdot 8}{126 \cdot 1 - n}$	$S = \dfrac{136 \cdot 8}{126 \cdot 1 + n}$
Fischer,	$\begin{cases} 12 \cdot 5^\circ \text{ R.} \\ 15 \cdot 625^\circ \text{ C.} \end{cases}$	$S = \dfrac{400}{400 - n}$	$S = \dfrac{400}{400 + n}$
Gay-Lussac,	4° C.	$S = \dfrac{100}{100 - n}$	$S = \dfrac{100}{100 + n}$
E. G. Greiner,	$\begin{cases} 12 \cdot 5^\circ \text{ R.} \\ 15 \cdot 625^\circ \text{ C.} \end{cases}$	$S = \dfrac{400}{400 - n}$	$S = \dfrac{400}{400 + n}$
Stoppani,	$\begin{cases} 12 \cdot 5^\circ \text{ R.} \\ 15 \cdot 625^\circ \text{ C.} \end{cases}$	$S = \dfrac{160}{160 - n}$	$S = \dfrac{160}{160 + n}$
Twaddle,	60° F.	$S = \dfrac{n + 200}{200}$	

C. = Centigrade. S = specific gravity.
F = Fahrenheit. n = degrees.
R = Réaumur.

the body weighed, if these happen to be the same in specific gravity, and, therefore, equal in volume, the error on one side of the scale balances that on the other. But, when the body weighed is water and the weights are of brass, about 8·5 times heavier than water, the volumes are nearly as 17 : 2, and, therefore, the apparent weight of the water is less than the true weight by an amount equal to about $1\frac{5}{7}$ths of the weight of air displaced by the water, and the apparent weight of any other liquid equal in volume to the water is short of the true weight by a like amount. Therefore, if W and w be the apparent weights of the water and the liquid respectively, and if W $+x$ be the true weight of the water, then $w + x$ is the true weight of the liquid, and the real specific gravity of the liquid is not $\dfrac{w}{W}$ but $\dfrac{w + x}{W + x}$.[1] x is always very small, and when W and w are nearly the same, $i.e.$ when the specific gravity is near unity, as in the case of most lubricating oils, the error amounts to only one or two points in the fourth decimal place, and may be neglected. But, in determining the specific gravity of a mixture of glycerol and water for the purpose of ascertaining the viscosity by means of the tables on pp. 140-143, the correction must be applied. As the weight of air varies with the temperature and pressure, the correction is not always exactly the same, but unless an error of $\pm$ ·00005 is too great (which is not the case here), the following table [2] will give the necessary correction without calculation :—

TABLE XXXIX.—CORRECTION FOR REDUCTION OF SPECIFIC
GRAVITY TO A VACUUM.

Sp. gr. found.	Correction to be added.	Sp. gr. found.	Correction to be added.
0·75	+ 0·00031	1·05	− 0·00006
0·80	+ 0·00025	1·10	− 0·00012
0·85	+ 0·00018	1·15	− 0·00018
0·90	+ 0·00012	1·20	− 0·00025
0·95	+ 0·00006	1·25	− 0·00031
1·00	+ 0·00000	1·30	− 0·00037

Change of Standard (Determination of Density).—To reduce the specific gravity of an oil or other liquid, compared with water at $t°$ C. as standard, to the specific gravity compared with water at 4° C. as standard $i.e.$ to ascertain the *density* of the liquid at $t°$—all that

[1] Alder Wright, "On Fluid Specific Gravities," *Jour. Soc. Chem. Ind.*, **xi.** (1892), p. 297.
[2] Dittmar, *Chemical Arithmetic*, vol. i. p. 111.

is necessary is to multiply the specific gravity at $t°$ by the density of water at $t°$ which is given in Table XL.[1]

TABLE XL.—DENSITIES OF WATER AT 4° C. (39·2° F.) TO 100° C. (212° F.). (*Rosetti.*)

°C.	°F.	Density D.	Diff.
4	39·2	1·00000	
5	41	·99999	-2
6	42·8	97	4
7	44·6	93	4
8	46·4	89	7
9	48·2	82	7
10	50·0	75	9
11	51·8	66	11
12	53·6	55	12
13	55·4	43	13
14	57·2	30	14
15	59	16	16
16	60·8	00	16
17	62·6	·99884	19
18	64·4	65	19
19	66·2	46	20
20	68	26	21
21	69·8	05	22
22	71·6	·99783	23
23	73·4	60	23
24	75·2	37	25
25	77	12	25
26	78·8	·99687	27
27	80·6	60	27
28	82·4	33	28
29	84·2	05	28
30	86	·99577	30
31	87·8	47	30
32	89·6	17	32
33	91·4	·99485	33
34	93·2	52	34
35	95	18	35

°C.	°F.	Density D.	Diff.
36	96·8	·99383	36
37	98·6	47	37
38	100·4	10	37
39	102·2	·99273	38
40	104	35	38
41	105·8	·99197	39
42	107·6	58	40
43	109·4	18	40
44	111·2	·99078	41
45	113	37	41
46	114·8	·98996	42
47	116·6	54	44
48	118·4	10	45
49	120·2	·98865	46
50	122	19	47
51	123·8	·98772	47
52	125·6	25	48
53	127·4	·98677	48
54	129·2	29	48
55	131	·98581	47
56	132·8	34	48
57	134·6	·98486	49
58	136·4	37	49
59	138·2	·98388	50
60	140	36	52
61	141·8	·98286	52
62	143·6	34	52
63	145·4	·98182	54
64	147·2	28	54
65	149·0	·98074	55
66	150·8	19	55
67	152·6	·97964	56

°C.	°F.	Density D.	Diff.
68	154·4	·97908	57
69	156·2	·97851	57
70	158	·97794	58
71	159·8	36	59
72	161·6	97677	59
73	163·4	18	60
74	165·2	·97558	60
75	167	·97498	60
76	168·8	38	61
77	170·6	·97377	61
78	172·4	16	61
79	174·2	·97255	61
80	176	·97194	62
81	177·8	32	62
82	179·6	·97070	63
83	181·4	07	64
84	183·2	·96943	64
85	185	·96879	64
86	186·8	15	64
87	188·6	·96751	64
88	190·4	·96687	65
89	192·2	22	66
90	194	·96556	66
91	195·8	·96490	67
92	197·6	23	67
93	199·4	·96356	68
94	201·2	·96288	69
95	203	19	70
96	204·8	96149	70
97	206·6	·96079	71
98	208·4	08	71
99	210·2	·95937	71
100	212	·95866	

At 60° F., D = 0·99907.   At 100° F., D = 0·99317.
70° F., D = 0·99803.   150° F., D = 0·98044.

[1] Taken, with slight alterations, from Dittmar's *Chemical Arithmetic*, vol. i. p. 107.

Example.—The sp. gr. of a mixture of glycerol and water at $\frac{20°}{20°}$ C. was found to be 1·1848; therefore, the sp. gr. at $\frac{20°}{4°}$ C., *i.e.* the density of the liquid, is 1·1848 × 0·99826 = 1·1828.

Alteration in the Densities of Lubricating Oils produced by Change of Temperature.—In order to determine the viscosity of a lubricating oil at any temperature, it is necessary to know the density of the oil at that temperature. At either 60° F. (15·5° C.) or 212° F. (100° C.) it is easy to determine the density, but at intermediate temperatures it is not always easy. The density may, however, be calculated nearly enough, when the densities at 60° F. and 212° F. are known.

In Table XLI. are given the densities at 60° F. and 212° F. of a number of lubricating oils, with the average differences for 1° F. and 1° C. It will be noticed that these differences are very nearly the same for all oils, and it is possible, without much error, to calculate the density of an oil at any given temperature between 60° F. and 212° F., if we know the density at 60° F., by means of the following formula :—

$$D = d - kt$$

Where, d = the density of the oil at 60° F.

$$k = \begin{cases} 0·000368 \text{ for a fixed oil.} \\ 0·000367 \text{ for a Scotch mineral oil.} \\ 0·000345 \text{ for a Russian mineral oil.} \\ 0·000350 \text{ for an American mineral oil} \end{cases}$$

t = the number of degrees above 60° F.
D = the required density.

The following examples show the degree of accuracy thus attainable :—

1. *Rape Oil.*

Density at　60° F. (determined)　　　　　　　　= 0·9151

Density at 100° F. (calculated) = 0·9151 − 0·000368 × 40 = 0·9004
Density at 100° F. (determined)　　　　　　　= 0·9002

Density at 150° F. (calculated) = 0·9151 − 0·000368 × 90 = 0·8820
Density at 150° F. (determined)　　　　　　　= 0·8818

2. *American Cylinder Oil.*

Density at　60° F. (determined)　　　　　　　= 0·8858

Density at 100° F. (calculated) = 0·8858 − 0·000350 × 40 = 0·8718
Density at 100° F. (determined)　　　　　　　= 0·8720

TABLE XLI.—TABLE SHOWING THE ALTERATION IN DENSITY OF
LUBRICATING OILS CAUSED BY RISE OF TEMPERATURE (*Archbutt*).

Description of Oil.	Density at		Difference per One Degree.	
	60° F. 15·5° C	212° F. 100° C.	Fahr.	Cent.
Animal and Vegetable Oils.				
Sperm oil,	0·87828	0·82290	0·000364	0·000656
Olive oil,	0·91586	0·85962	0·000370	0·000666
Rape oil	0·91506	0·85948	0·000365	0·000659
Tallow,	0·87840 at 150° F.	0·85572	0·000366	0·000680
Castor oil,	0·96240	0·90500	0·000378	0·000659
Neutral wool fat,	0·91370	0·89092	0·000367	0·000660
		Average	0·000368	0·000663
Scotch Mineral Oils.				
'865,'	0·86826	0·81160	0·000373	0·000671
'89,'	0·89054	0·83560	0·000361	0·000651
		Average	0·000367	0·000661
Galician Mineral Oils.				
Light (pale) machinery oil,	0·88854	0·83388	0·000359	0·000646
Heavy (pale) machinery oil,	0·89610	0·84322	0·000348	0·000626
		Average	0·000354	0·000636
Russian Mineral Oils.				
Light machinery and spindle oil,	0·89782	0·84420	0·000353	0·000635
Medium (pale) machinery oil,	0·90960	0·85684	0·000347	0·000625
Heavy (pale) engine and machinery oil,	0·90850	0·85682	0·000340	0·000612
Heavy (dark) axle oil,	0·90930	0·85692	0·000344	0·000619
Extra heavy (pale) engine and machinery oil,	0·90852	0·85682	0·000340	0·000612
		Average	0·000345	0·000620
American Mineral Oils				
Spindle oil ('Pale 885'),	0·88436	0·82978	0·000359	0·000647
„ „ ('Pale 860/70'),	0·86766	0·81384	0·000354	0·000638
Light machinery oil ('900/7')	0·90082	0·84694	0·000354	0·000638
'Globe' oil (dark),	0·88019	0·82726	0·000348	0·000627
Light machinery oil ('905/10'),	0·90540	0·85258	0·000347	0·000626
'Solar red' engine oil,	0·91620	0·86242	0·000354	0·000637
'Bayonne' engine oil,	0·91132	0·85790	0·000351	0·000633
'Special red' engine oil,	0·93493	0·88172	0·000350	0·000630
Medium (dark) machinery oil,	0·88390	0·82910	0·000361	0·000649
'Galena' axle oil,	0·90790	0·85552	0·000345	0·000621
Heavy (pale) machinery oil,	0·90124	0·84930	0·000342	0·000616
Filtered cylinder oil ('Valvoline'),	0·88915	0·83769	0·000338	0·000609
„ „ ('F.F.F.'),	0·88982	0·83932	0·000332	0·000598
Dark cylinder oil ('A'),	0·89908	0·84414	0·000361	0·000651
„ „ ('N),	0·89832	0·84440	0·000350	0·000650
„ „ ('Locomotive'),	0·89974	0·84732	0·000345	0·000621
Dark filtered cylinder oil ('N'),	0·90942	0·85556	0·000354	0·000637
		Average	0·000350	0·000631

TABLE XLII.—SPECIFIC GRAVITIES AT 60° F. (15·5° C.) OF SOME FIXED OILS, FATS, WAXES, ETC.

Class.	Name of Oil, etc.	Specific Gravity at 60° F.
Vegetable Non-drying Oils and Fats	Olive oil,	{ 0·914 -0·917 { Rarely 0·918
	Olive kernel oil,	0 918 –0 919
	Hazel nut oil,	0·915 -0·917
	Ben oil,	0·912 -0·920
	Arachis (earthnut) oil,	0·911 -0·926
	Castor oil,	0·959 -0 968
	Japan wax,	0·970 0·993
	Coconut oil (neutral),	0 959
	Palmnut oil („),	0·978
	Palm oil,	0·921 -0·925
	Cottonseed stearin,	0·919 -0·923
Vegetable Semi-drying Oils.	Rape oil,	0·9132 0·9165
	Ravison oil,	0·918 -0·922
	Mustard oil (white),	0·913 0·916
	„ „ (black),	0·916 -0·919
	Curcas oil,	0·919 -0·921
	Cottonseed oil,	0 921 -0 926
	Sesamé oil,	0·923 -0·926
	Brazil nut oil,	0·918 -0·919
	Beech nut oil,	0 920 0·923
	Maize oil,	0·921 -0·928
	Cameline oil,	0·920 -0·926
Vegetable Drying Oils.	Linseed oil,	0·931 -0 938
	Hempseed oil,	0·925 -0·931
	Poppyseed oil,	0·924 -0·927
	Walnut oil,	0·925 -0 927
	Nigerseed oil,	0·925 -0·928
	Sunflower oil,	0 924 -0·926
Animal Oils and Fats.	Neatsfoot oil,	0·914 -0·919
	Lard oil,	0·913 -0·919
	Horsefoot oil,	0·920 -0 927
	Tallow (mutton),	0·937 -0·953
	„ (beef),	0·943 -0 953
	Bone fat,	0 914 -0·916
	Lard,	0·931 -0 938
	Horse fat,	0·916 -0·922
Marine Animal Oils and Fluid Waxes.	Sperm oils (Southern and Arctic),	0·879 -0·884
	Porpoise jaw oil,	0·926
	Porpoise body oil,	0·926 -0·935
	Dolphin body oil,	0·927
	Whale oil,	0 916 -0·927
	Seal oil,	0·924 -0·927
	Cod liver oil,	0·922 -0·933
	Other fish liver oils,	0·910 -0·931
	Menhaden oil,	0·927 0 933
	Sardine (including Japan fish) oil,	0·916 0·934
Waxes (solid).	Wool fat, crude (18·4 % free fatty acids),	0·959
	„ „ (neutral),	0 954
	Spermaceti,	0·905 0·960
	Beeswax,	0·958 ·975
	Carnauba wax,	0·990 -0·999
Blown Oils.	Blown rape and ravison oils,	0 955 -0·972
	Blown cottonseed oil (' Lardine '),	0·967 -0·985
Miscellaneous.	Vaseline,	0·85 -0·909
	Paraffin wax (according to melting point),	0·824 -0·940
	Cerasin (refined ozokerit)	0·918 -0·922
	Colophony,	1·045 -1·108

TABLE XLI.—TABLE SHOWING THE ALTERATION IN DENSITY OF LUBRICATING OILS CAUSED BY RISE OF TEMPERATURE (*Archbutt*).

Description of Oil.	Density at		Difference per One Degree.	
	60° F. 15·5° C	212° F. 100° C.	Fahr.	Cent.
Animal and Vegetable Oils.				
Sperm oil,	0·87828	0·82290	0·000364	0·000656
Olive oil,	0·91586	0·85962	0·000370	0·000666
Rape oil	0·91506	0·85948	0·000365	0·000659
Tallow,	0·87840 at 150° F.	0·85572	0·000366	0·000680
Castor oil,	0·96240	0·90500	0·000378	0·000659
Neutral wool fat,	0·91370	0·89092	0·000367	0·000660
		Average	0·000368	0·000663
Scotch Mineral Oils.				
'865,'	0·86826	0·81160	0·000373	0·000671
'890,'	0·89054	0·8356	0·000361	0·000651
		Average	0·000367	0·000661
Galician Mineral Oils.				
Light (pale) machinery oil,	0·88854	0·83388	0·000359	0·000646
Heavy (pale) machinery oil,	0·89610	0·84322	0·000348	0·000626
		Average	0·000354	0·000636
Russian Mineral Oils.				
Light machinery and spindle oil,	0·89782	0·84420	0·000353	0·000635
Medium (pale) machinery oil,	0·90960	0·85684	0·000347	0·000625
Heavy (pale) engine and machinery oil,	0·90850	0·85682	0·000340	0·000612
Heavy (dark) axle oil,	0·90930	0·85692	0·000344	0·000619
Extra heavy (pale) engine and machinery oil,	0·90852	0·85682	0·000340	0·000612
		Average	0·000345	0·000620
American Mineral Oils				
Spindle oil ('Pale 885'),	0·88436	0·82978	0·000359	0·000647
,, ,, ('Pale 860/70'),	0·86766	0·81384	0·000354	0·000638
Light machinery oil ('900/7')	0·90082	0·84694	0·000354	0·000638
'Globe' oil (dark),	0·88019	0·82726	0·000348	0·000627
Light machinery oil ('905/10'),	0·90540	0·85258	0·000347	0·000626
'Solar red' engine oil,	0·91620	0·86242	0·000354	0·000637
'Bayonne' engine oil,	0·91132	0·85790	0·000351	0·000633
'Special red' engine oil,	0·93493	0·88172	0·000350	0·000630
Medium (dark) machinery oil,	0·88390	0·82910	0·000361	0·000649
'Galena' axle oil,	0·90790	0·85552	0·000345	0·000621
Heavy (pale) machinery oil,	0·90124	0·84930	0·000342	0·000616
Filtered cylinder oil ('Valvoline'),	0·88915	0·83769	0·000338	0·000609
,, ,, ('F.F.F.'),	0·88982	0·83932	0·000332	0·000598
Dark cylinder oil ('A'),	0·88908	0·84414	0·000361	0·000651
,, ,, ('N'),	0·89832	0·84440	0·000360	0·000650
,, ,, ('Locomotive'),	0·89974	0·84732	0·000345	0·000621
Dark filtered cylinder oil ('N'),	0·90942	0·85556	0·000354	0·000637
		Average	0·000350	0·000631

C.—FLASHING-POINT.

All lubricating oils when sufficiently heated give off vapour. The *'flashing-point'* is the temperature at which the amount of vapour given off is sufficient to form an inflammable or mildly explosive mixture with the air over the surface of the oil, so that on the application of a flame the gaseous mixture ignites and burns with a momentary flash. As the temperature of the oil rises, more vapour is given off, and when the production of vapour is rapid enough to maintain a continuous flame, the oil takes fire and burns; the temperature at which this occurs is called the 'firing-point,' 'fire-test,' or 'burning-point' of the oil. The determination of these points, more especially of the flashing-point, is of great importance in the examination of lubricating oils, because oils of low flashing-point are unsafe to use.

An important difference exists in the behaviour of the two classes of lubricating oils when heated. The fixed (animal and vegetable) oils do not evaporate, and no vapours are given off (except, possibly, traces of moisture) on heating them, until the oils begin to decompose; the vapours then given off are products of the destructive distillation of the oil, which requires a fairly high temperature to bring it about, and consequently the flashing-points of such oils are high (over 400° Fahr.). On the other hand, all mineral or hydrocarbon oils evaporate when heated, and the temperature at which sufficient vapour is given off to cause a flash depends upon what hydrocarbons are contained in the oil. Mineral lubricating oils do not, as a rule, contain the more volatile hydrocarbons of petroleum, which belong properly to the naphtha and burning oil fractions, but *'natural'* oils, and imperfectly refined oils, may give off vapour at temperatures low enough to be dangerous.

Owing to improved methods of manufacture, and greater care in refining, low-flashing mineral oils are more rarely met with than formerly; nevertheless, in textile mills, and wherever danger from fire has to be guarded against, the precaution of determining the flashing-point of the lubricating oil must never be neglected. In 1883, Veitch Wilson stated that he had met with one sample of oil offered for lubrication which flashed at the ordinary temperature of the atmosphere, and several which flashed at 150° to 200° F. Ordway, who examined a large number of oils in actual use in cotton mills in the United States, found several which flashed at 180° F., and a larger number which flashed below 212° F. The use of such dangerous oils would not now be tolerated, and a flashing-point of 340°–350° F. is regarded by oil manufacturers, users, and insurance companies, as a standard of safety to which all oils for indoor machinery ought to attain. For outdoor machinery, a limited quantity of oil is still sold having a flashing-point of 200°–210° F.

It is seldom necessary to determine the flashing-points of fixed oils, but, as a means of detecting or confirming adulteration with light mineral oil, the test is sometimes useful.

It is a usual practice to determine the flashing-point of cylinder oils, on the ground that oils of high flashing-point may be expected to evaporate less in the cylinders than those of lower flashing-point. But there is no necessary relation between the flashing-point and the volatility of lubricating oils, and in comparing together mineral oils of different origin (e.g. Russian and American oils) the less volatile oil may even have the lower flashing-point (see Table XLVII. on p. 194). In the authors' opinion, the flashing-point of cylinder oils is a test which might with advantage be dispensed with and replaced by a quantitative determination of the amount lost by evaporation under definite conditions (see Volatility, p. 191).

Determination of the Flashing-point.

'Open Test.' Flashing- and Firing-Points.—The method formerly used, and still preferred by some, for determining the flashing- and burning-points of lubricating oils, known as the 'open test,' consists in heating some of the oil, in which the bulb of a thermometer is immersed, in a small open metallic cup, a porcelain crucible embedded in sand, or some equivalent contrivance, and passing a small flame across the surface of the oil at frequent intervals. When the amount of vapour given off is enough to form an inflammable mixture with the air, a pale blue flash occurs on application of the test flame, and the temperature at which this flash is first observed is the flashing-point of the oil. To determine the firing-point, the testing is continued until on applying the test flame to the surface of the oil it takes fire and burns continuously.

'Closed Test.'—A little experience is sufficient to show that the above rough method of determining the flashing-point is incapable of giving uniform results. The temperature at which the first flash is obtained depends upon the presence or absence of air currents, the rate of heating, the size and shape of the vessel used, the distance of the test-flame from the oil surface, etc. One of the authors was among the first to abandon the 'open' in favour of the 'closed test,' now almost universally employed for testing lubricating as well as burning oils. For this purpose a brass cup furnished with a close-fitting lid and slide (an exact copy of the Abel petroleum cup) was constructed with brazed joints, so as to withstand heating to a high temperature, and instead of the outer water-bath a thick cast-iron cup on feet was made in which the test-cup fitted loosely. Heat was so applied to the cast-iron body as to cause the temperature of the oil to rise rapidly at first, and when near the flashing-point the rate of heating was reduced to about two degrees per minute, and the gas testing-flame was applied every two degrees by opening the slide, exactly as in the Abel test. Improved forms of apparatus have since been devised by Pensky and Martens and by Gray, in which the important addition of a stirrer has been introduced, which enables the heating of the oil to be conducted much more rapidly without impairing the uniformity of the results.

The Pensky-Martens Test Apparatus.—This apparatus, shown in fig. 59, consists of the brass cup, A, with flange B, which drops loosely into the cast-iron body, C, the flange resting upon the dome-shaped brass shield, D. The position of the cup is fixed by studs, EE, which engage in slots in the flange. The cup has a close-fitting lid with a revolving perforated slide actuated by the spring lever H, by turning which the openings in the slide are brought over corresponding openings in the lid, and the little gas testing-flame is at the same time caused to dip through the central opening into the air-space above the oil in the cup, igniting the mixture of air and vapour as soon as it becomes inflammable. The lid also carries the stirrer S, with two sets of vanes, one in the oil and the other in the air space ; also the thermometer, T.

FIG. 59.

In making a test, the cup is placed upon a level surface and filled with oil to the mark ; it is then placed in the test-apparatus, and the lid is put on. The small test-flame having been lighted and turned down until the luminous tip has almost disappeared, the oil is gradually heated up by means of the burner K, the wire net, L, being swung out of the way. The flame at first used is large enough to heat the oil rapidly, but as soon as the test-flame when lowered into the cup shows a tendency to enlarge, the heat is moderated and the wire net may be swung over the flame. The stirrer is now worked so as to keep the oil as well as the vapour and air thoroughly mixed, and the test-flame is applied at every two degrees' rise of temperature, until the flashing-point is reached. The temperature of the oil towards the end of the experiment may rise at the rate of 10 degrees C. per minute (see below) so long as the oil is kept thoroughly stirred, but the stirrer must not be worked while the test-flame is being applied. The application of the flame should occupy about two seconds, three half-seconds being occupied in opening the slide and the remaining half-second in closing it. Oils containing water must be dried by filtering through dry filter paper or a column of coarsely-crushed calcium chloride before being tested, as the presence of much moisture causes very irregular and incorrect results to be obtained.
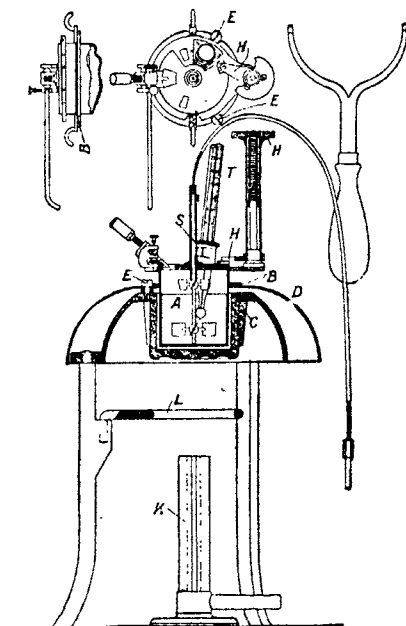
¶ This apparatus has been subjected to an elaborate series of tests by Holde. By making repeated tests with oils of different flashing-points, he has shown

that rapid heating with continuous, vigorous stirring, gives the same results as slow heating without stirring, and when testing the same oil several times the results agreed within 2 or 3 degrees C. ($3\frac{1}{2}°$ to $5\frac{1}{2}°$ F.), even when the thermometer rose as rapidly as 10° C. ($=18°$ F.) per minute towards the end of the experiment. According to Holde, a rise in temperature of 12° C. ($=22°$ Fahr.) per minute is permissible. The size of the testing-flame does not influence the result appreciably, but it is not desirable to use too large a flame, otherwise the flash may not be plainly seen. Filling the oil holder above the mark, and so reducing the air space, tends to lower the flashing-point. Thus, Holde found that with an oil flashing at about 155° C. ($=311°$ F.) the mean flashing-point differed 4° C. ($=7.2°$ F.) according to whether the cup was filled 1 cm. below or 1 cm. above the mark. Accordingly it has been proposed by Aisinmann[1] that as an oil of high flashing-point will expand during the test more than an oil of low flashing-point, the cup should not be filled to the same mark with all oils, but the quantity used should be such as will by expansion have reached to the mark at the flashing-point. Thus, taking 0·00068 (per 1° C.) as the coefficient of expansion of Russian lubricating oils, the total expansion per 75 c.c. of oil (the quantity used in the Martens cup) is 0·5 c.c. per 10° C. Therefore, the quantity of oil to be used in order to ascertain the correct flashing-point of an oil flashing at, say, 200° C. should be, according to Aisinmann, not 75 c.c., but (at an initial temperature of 20° C.) —

$$75 - \left(\frac{200 - 20}{10}\right) \times 0.5 = 66 \text{ c.c.}$$

Correcting the volume in this way, Aisinmann obtained the following results :—

TABLE XLVI.

Usual Volume.	Corrected Volume			Difference °C.	Reduction in Volume of Oil used. c.c.
	Flashing-point °C.				
151°	153°	154°	...	2·5°	6·55
193°	200°	200°	...	7·0°	8·65
257°	266°	268°	268°	10·3°	11·85

To adopt Aisinmann's proposal would greatly increase the labour of determining the flashing-point, without any equivalent advantage. The test, however performed, is an empirical one, and all that is required is the adoption of a uniform system of testing, so that disputes between manufacturers and users may be avoided. The principal object of determining the flashing-point is the detection of dangerous and wastefully volatile oils, and from this point of view the method of testing which gives the lowest result is to be preferred.

Holde[2] has since published further experiments showing that with oils flashing between 172° and 241° C. (342° and 466° F.) a variation of even as much as 13 c.c. below the normal filling of the cup does not alter the flashing-point more than 1°-1·5° C. (1·8°-2·7° F.).

[1] *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 284.   [2] *Ibid.*, xvi. (1897), p. 322.

Gray's Test Apparatus.—This (fig. 60) is an adaptation of the Pensky-Martens revolving slide and stirrer to the Abel cup. The inventor states[1] that in working with the Pensky apparatus he found the results under varied conditions to be excellent, and was struck with the idea that the instrument might be simplified and made more suitable for every-day work in the technical laboratory. He therefore devised a modified apparatus, which is thus described :—

"The stirrers, consisting of two sets of vanes, one in the oil and the
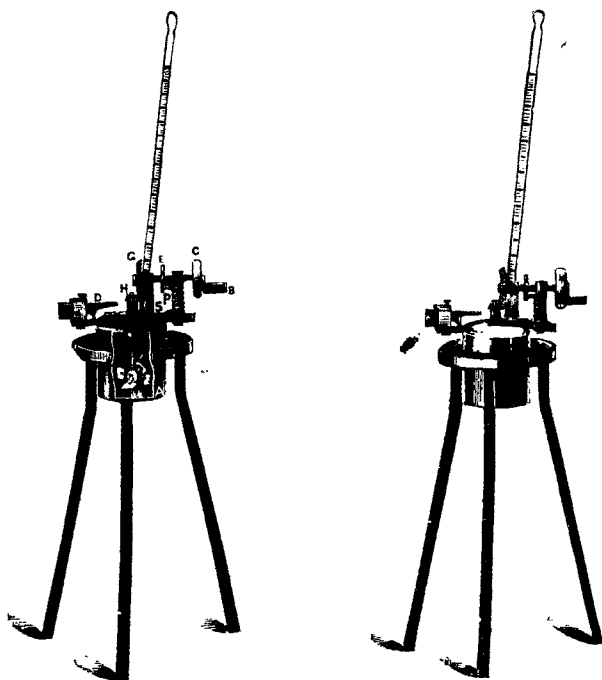
FIG. 60.—Gray's Tester.

other in the vapour space, are attached to a vertical shaft passing through the cover and terminating at the top in a small bevelled wheel, the bevel of which is milled. A horizontal shaft (carried on two supports) .erminates at one end with a bevelled wheel, gearing with the one on the stirrer shaft, and at the other end with a disc carrying a small handle with which to rotate the shaft. This shaft also carries a collar with two pins projecting about ¼ in. at diametrically opposite points. By sliding the shaft slightly to the right, the bevel wheels are put out of gear, and the pins projecting from the collar are drawn into position for actuating the testing arrangement. This consists of a sliding cover on the top of the lid proper, so

Jour. Soc. Chem. Ind., x. (1891), p. 348.

arranged that when the former is moved it depresses the test light to the proper point, and brings the orifices opposite those on the fixed lid. There are three orifices, one, at which the test light is applied, the other two, situated one at either side of it, being for the admission of air. It will thus be readily seen that the change from stirring to testing, and *vice versa*, can be instantly performed.

" The results obtained by this apparatus are identical with those obtained by the Pensky-Martens. They are not affected by the source of heat, a naked flame giving the same results as the sand bath. It is immaterial what the rate of heating is, provided it is not too rapid to prevent a correct reading of the thermometer. I prefer to reduce the rate of heating when nearing the point at which the oil is expected to flash. The stirrers do not require to be worked continuously, but merely at intervals. I find it advisable to stir more frequently when the rate of heating is fast."

In the latest form of this apparatus, the oil-cup does not fit directly into the tripod stand, as shown in the figure, but into a cast-iron vessel which is supported on the tripod, somewhat after the same manner as in the Pensky-Martens apparatus.

D.—**VOLATILITY**.

The property of being volatile or capable of evaporating without decomposition distinguishes the hydrocarbon oils from the fixed oils, but the temperature at which evaporation takes place depends upon the nature of the hydrocarbons contained in the oil. In any case the oil does not evaporate unchanged, for those hydrocarbons which are most volatile pass off first, leaving the less volatile hydrocarbons as a more or less viscid residue.[1] If the oil be a mixed one, the fatty component remains also, and the composition and character of the original oil may thus become entirely changed. The best qualities of machine oil scarcely evaporate in use, but at the high working temperatures of steam-cylinders all mineral lubricating oils evaporate. It is obvious that an oil which evaporates to a serious extent at the working temperature cannot be an economical lubricant, since all that evaporates is lost and the remainder may form a viscid or even a dry residue on the bearing. Notwithstanding its importance, this property of lubricating oils seldom receives the attention it deserves, a high flashing-point being generally regarded as sufficient evidence of the durability of even cylinder oil. Veitch Wilson long ago called attention to this anomaly, pointing out that the significance attached to the flashing-point should be limited to what it really indicates, viz., the relative safety of an oil, whilst the tendency to evaporate should be ascertained by measuring the actual loss of weight under definite conditions of time and temperature.

Determination of Volatility.—The usual method of determining the volatility of mineral lubricating oil is to place a weighed quantity, 0·5-1·0 grm., in a shallow dish or watch glass and expose it in a water- or air-oven for a certain number of hours, noting the loss of weight. Veitch Wilson states that machine oils when exposed in

[1] At temperatures above 200° C. the heavy hydrocarbons decompose.

this manner for ten hours at the temperature of the ordinary water-
oven (about 212° F.) should not lose weight, whilst Hurst states that
the loss in twenty-four hours should not exceed 0·25 to 0·5 per cent.
Cylinder oils are tested similarly in an air-oven heated to the tem-
perature of the steam cylinder.

Archbutt has pointed out that the loss of weight sustained by an
oil when tested in this manner must depend upon the number of times
the air of the oven is changed during the test, and he has proposed
the following method of testing in which the receptacle containing
the oil is heated in a tube to a known temperature whilst a current of
air heated to the same temperature is passed over the oil.
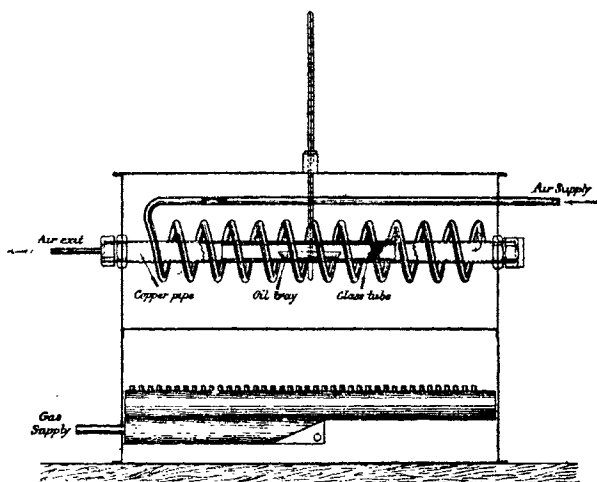
FIG. 61.

Archbutt's Vaporimeter (fig. 61) consists of a straight copper tube, ⅞ inch
in internal diameter and 1 or 2 feet long, having a branch tube ¾ inch in
diameter and about 10 feet long, brazed into it near one end and coiled
around the straight tube as shown in the figure. This tube and coil are
fixed in a rectangular air-oven made of tinned sheet iron, the sides and top
of which are covered with asbestos millboard. The oven is heated by a
row of small gas jets, and a thermometer is fixed with its bulb close to the
middle of the wide copper tube. The ends of this tube which project
beyond the oven are closed by brass screw caps, one of which, at the air-exit
end, is perforated and carries a narrow tube in the centre. Air or steam
admitted to the coiled tube, after becoming heated in the coil to the
temperature of the oven, passes over the oil in the wide tube and escapes
through the short tube in the cap. The oil is contained in a platinum tray,
3 in. long by ½ in. wide by ¼ in. deep, which for convenience of manipula-
tion is placed in a glass tube which just slides easily within the copper tube
and serves as a carrier.

The current of air is maintained at the constant speed of 2 litres per minute by means of the simple regulator shown in fig. 62 The air enters the regulator at A, and a slight excess is kept continually escaping at the lower end of the wide tube B, which is immersed to the depth of 3 inches in water. The supply is taken from the branch C, the orifice of which is reduced until just large enough to pass 2 litres per minute against atmospheric pressure under the 3 inches head of water.[1]

The quantity of oil used for a test is 0·5 grm, which forms a thin layer on the bottom of the platinum tray, and the oil is exposed to the air-current for exactly one hour. The temperature of the oven is varied to suit the requirements of the test. For cylinders working at 160 lbs. pressure per sq. in., the oil is tested at 370° F., and should not lose more than from 0·5 to 1 per cent. in weight in the time specified (one hour). At 400° F. (= 235 lbs pressure) the loss of weight of cylinder oils is about two and a half times as great as at 370° F.

If it be desired to use a current of steam instead of air, the inlet end of the vaporimeter is connected to a flask or boiler, and the outlet to a condenser. The gas flame under the boiler is regulated so as to distil a definite quantity of water in the hour, 100 c.c. being a convenient volume, though 92 c.c. is the volume required to give a current of steam nearly equal to the above-mentioned air current. The boiler is detached, all the steam is blown out of the tube, and the platinum tray containing the oil is inserted.   After waiting a few

Fig. 62.

minutes for the tray of oil to become heated up, the steam current is turned on. If the tray be inserted without first blowing out the steam, water condenses upon the tray, the oil creeps over the edge, and the test is spoiled.

The figures in the following table show the kind of results obtained by this test. All the samples of oil tested were pure mineral oils, the first three being described as cylinder oils. and the last two as machine oils.
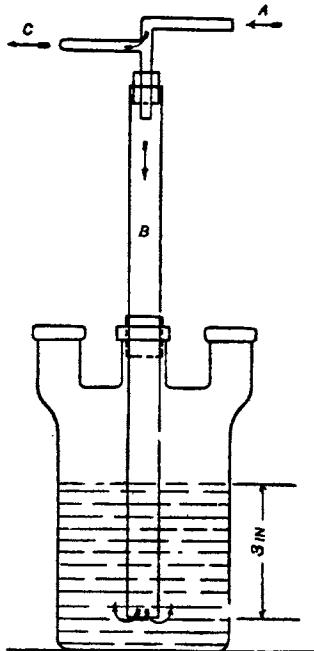
[1] This is done by connecting the exit-tube C, by means of a flexible tube and cork, to the neck of a bell-jar of known capacity, full of water, sunk in a bucket of water. As the air passes into the bell-jar, the latter is gradually raised so as to maintain the same water level within and without the jar, and the orifice of the branch C is made of such dimensions as will allow the jar to fill in the calculated time.

TABLE XLVII.—FLASHING-POINTS AND VOLATILITY COMPARED.

No.	Description.	Sp. Gr. at 60° F.	Flashing-Point (Pensky-Martens) F.	Loss of Weight in One Hour at 370° F.	
				In Air; 2 Litres per minute.	In Steam; 100 c.c. of Water condensed per hour.
1	American cylinder oil, .	0·902	585°	Per cent. 0·12	Per cent ...
2	„ „ „	0·898	512° {	0·54 ⎰ 0·56 ⎱	0·70 0·46
3	„ „ „	0·893	424°	4·18	0·68 ...
4	American machine oil,	0·897	402° ⎰	16·8 ⎰ 16·3 ⎱	18·1 17·6
5	Russian machine oil, .	0·909	380° ⎰	14·7 ⎰ 14·3 ⎱	16·0 16·7

As the volume of steam passed over the oils in these experiments was about 8 per cent. in excess of the volume of air, the figures in the last two columns are not comparable. But, if we assume the rate of evaporation to have been proportional to the volume of steam, and correct the results accordingly, the following numbers are obtained, which agree so closely as to show that the rate of evaporation in both steam and air is the same.

Average Loss per cent.	No. 2.	No. 4.	No. 5.
In air current, ...	0·55	16·55	14·50
In steam current of same volume (calculated), ...	0·57	16·32	15·04

It is evident that no simple relation exists between the volatility of an oil and the flashing-point. It is true of the four American oils that as the flashing-point falls the volatility increases ; but the Russian oil flashing at 380° lost less by evaporation than the American oil flashing at 402°. The two oils flashing at over 500° F. both lost less than 0·6 per cent., though there is a difference of 73° F. in their flashing-points ; on the other hand, No. 3, which flashed 88° F. below No. 2, lost over 4 per cent., and No. 4, which flashed at only 22° F. lower still, lost over 16 per cent. (For some further results see p. 310.)

E.—SETTING-POINT OR COLD TEST OF LUBRICATING OILS.

The effect of cold upon lubricating oils is not the same as upon simple fluids such as water, glycerin, etc. The latter have fixed and accurately ascertainable freezing-points, at which a complete change from the liquid to the solid state takes place, but lubricating oils, which are mixtures of bodies of various melting-points, behave like solutions, and frequently deposit some portion of their constituents before the whole mixture solidifies. Thus, olive and lard oils deposit a solid fat, sperm oil deposits spermaceti, and some hydrocarbon oils deposit paraffin. The 'setting-point' of an oil will, therefore, vary according to whether it be regarded as the temperature at which solid matter commences to separate, or the temperature at which the oil completely loses its fluidity. The setting-point of Scotch mineral oils is considered to be the temperature at which the separation of solid paraffin is observed to commence; but Russian oils, some pale American oils of high viscosity, and all dark-coloured or opaque oils, which either deposit no paraffin or in which the separation cannot be seen, are considered to have reached their setting-point when they cease to flow. The low setting-points of Russian and of some American lubricating oils, which deposit little or no paraffin, is characteristic, and serves to distinguish them from most of the American and from the Scotch oils; Russian oils, when cooled, simply become more and more viscous until the setting-point is reached. Among vegetable lubricating oils, castor and almond oils have the lowest solidifying-points.

Very erroneous conclusions regarding the setting-point of an oil may be formed unless sufficient *time* be allowed in making the test. This is especially true of fixed oils. Thus Salkowsky [1] found that a cod-liver oil, which remained perfectly clear when cooled for a short time to $-15°$ C., became quite solid after several hours' exposure to $-4°$ C. The subject has been more fully investigated by Holde. [2] The solidification of such oils is promoted by stirring, and by adding to the fluid oil a fragment of the same oil in a frozen state. Mineral oils assume their permanent state for any given temperature much more rapidly than the fixed oils, and, except when testing by the Scotch method (see below), they should not be stirred, as the network of solid hydrocarbons, which sometimes causes such oils to set before they have wholly solidified, is broken up by the stirring, and the setting-point is thereby lowered. Mineral lubricating oils frequently undergo a change in their solidifying points by previous heating, and it is, therefore, important that the portion used for the setting-point determination should not have been recently used for any other test which has involved heating above the atmospheric temperature.

[1] *Jour. Soc. Chem. Ind.*, vii. (1888), p. 37.
[2] *Ibid.*, ix. (1890), p. 112 ; also xv. (1896), pp. 138 and 90.

Determination of the Setting-Point.—The Scotch Method for ascertaining the temperature at which a mineral oil commences to deposit paraffin is as follows[1]:—The oil is poured to the depth of about 2 inches into a thick-walled test-tube about 1¼ inches in diameter, and the tube is immersed in a freezing mixture and slowly stirred 1 y a thermometer until it has been cooled down considerably below the temperature at which solid paraffin first appears. The tube is then removed from the freezing-mixture, wiped, and held up between the eye and a window, and, whilst the oil is constantly stirred with the thermometer, the temperature at which the last trace of solid paraffin disappears is read off. This operation is repeated with the same sample of oil until two experiments give concordant results, and the temperature so found is the setting-point of the sample.

Archbutt's Method for determining, approximately, the temperature at which an oil ceases to flow is carried out in a refrigerator (fig. 63), consisting
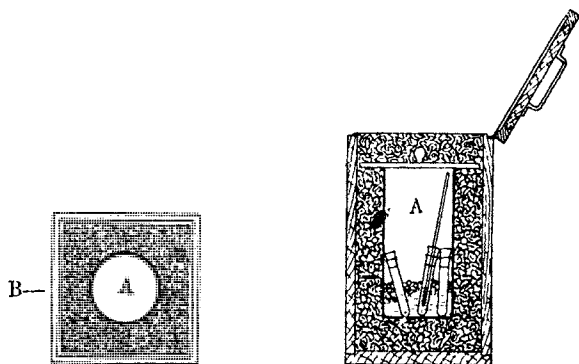
FIG. 63.

of a cylindrical leaden jar A, 6 inches in diameter and 14 inches in depth, with a flat bottom, contained in a wooden box B, measuring 12 inches square inside and 20 inches deep. The space between the leaden jar and the box is filled with dry cotton waste; 3 inches of waste are placed below the jar, and the top of the jar is covered by a loose wooden lid on which a layer of cotton waste is placed. The box has a hinged lid. The oils to be tested are poured to the depth of about 2 inches into glass specimen tubes measuring 6 inches in length by about ¾ inch in internal diameter, and the tubes are corked. A similar tube containing Russian lubricating oil of low viscosity and setting-point is used to contain the thermometer, which is passed through a perforation in the cork and has its bulb immersed in the oil.

About 2 inches in depth of crushed ice having been placed in the jar, the tubes of oil are immersed in the ice and left there for at least one hour. They are then taken out one by one and examined, and any oils which will not flow when the tube is held in a horizontal position and lightly tapped on the box are reported as having set in ice, or are placed aside for further

[1] *Jour. Soc. Chem. Ind.* (x.), 1891, 347.

experiment. The remainder are returned to the ice after this has been mixed, by thorough stirring, with sufficient powdered salt to lower the temperature about 5° F. The quantity to add is soon learned by experience. After twenty minutes' exposure to the lower temperature the tubes are again examined, any oils which have now set are taken out, and the temperature is read off on the thermometer. The addition of salt is repeated, and the gradual lowering of temperature with examination of the oils every twenty minutes is continued until the last oil has set, or until the temperature can be reduced no further. In this way the setting-point of an oil is ascertained within 5° F. A closer approximation can be made, if desired, by a second experiment, in which the temperature, when near the setting-point, is more gradually lowered. The setting-points of oils which solidify at temperatures above that of melting ice may be ascertained by placing the tubes in water at the temperature of the laboratory, and then gradually lowering the temperature of this water by the addition of small quantities of ice until the setting-point of the oil has been reached. Animal and vegetable oils must be stirred frequently, and the lowering of the temperature must be more gradual than in the case of mineral oils.

Hofmeister's Method.—The special feature of this method is the use, as freezing liquids, of saline solutions of such strength that they are saturated at their freezing-points; such solutions when partially frozen remain constant in temperature until they have become entirely liquefied or solidified, and are thus very convenient for keeping the temperature of an oil constant for a length of time. The following solutions may be used :—

TABLE XLVIII. —SALINE FREEZING SOLUTIONS.

Salt	Parts of Salt per 100 parts of Water.	Freezing-points of the Solutions.	
		Fahr	Cent.
Potassium sulphate, ...	10	28·6°	− 1·9°
Sodium carbonate crystals, .	20	28·4°	− 2·0°
Potassium nitrate, . . .	13	26·9°	− 2·85°
Potassium nitrate, . . Sodium chloride, . .	13 } 3 3 }	23·0°	− 5·0°
Barium chloride, . .	35·8	16·3°	− 8·7°
Potassium chloride, .	30	12·4°	− 10·9°
Ammonium chloride, .	25	4·3°	− 15·4°
Ammonium nitrate, . .	45	1·85°	− 16·75°
Sodium nitrate, . .	50	0·05°	− 17·75°
Sodium chloride, . .	33	− 4·3°	− 21·30°

A solution selected from the above list is placed in the vessel a (fig. 64), and about 4 c.c. of the oil to be tested are placed in one of the tubes h immersed in the solution. A freezing-mixture of ice and salt is placed in the outer vessel b. As soon as the temperature of the solution in a has fallen to its freezing point, if it does not commence to crystallize it is caused to do so by stirring, or by dropping in a small portion of the same solution which has been previously frozen in a test-tube. The temperature of the liquid in a, and therefore of the oils in tubes hh, will now remain constant

so long as the liquid remains only partially frozen, and to maintain it in this condition and prevent complete solidification from taking place, all that is necessary is to lift the vessel, a, out of the freezing mixture, occasionally, for a few minutes. After the lapse of one or two hours, the tubes of oil are lifted out of the bath, and any oils which do not flow on inclining the tubes are
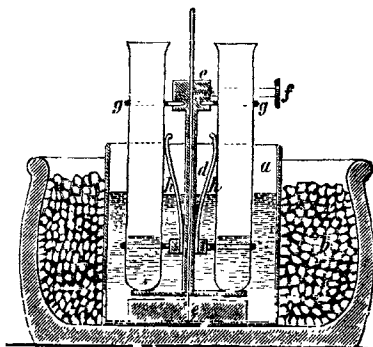
Fig. 64.

considered to have set at the temperature of the bath. The remainder are then tested in a solution freezing at a lower temperature. The standard liquids are preserved for use in stoppered bottles. This is a scientific method for determining accurately the effect on oils of prolonged exposure at low temperatures.
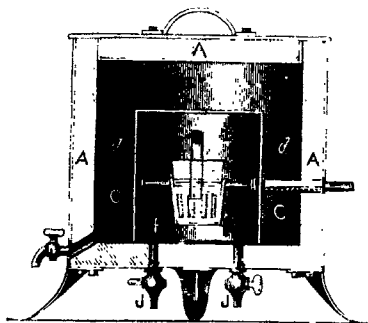
Fig. 65.

Schultz's Method.—In this method, used in Germany, the oil is cooled until of such consistency that when subjected to a fixed pressure in a tube of specified diameter it will flow at a definite minimum speed. The oil to be tested is introduced into a glass U-tube, 6 mm. in internal diameter, which is filled to a depth of 30 cm. in each limb. Several such tubes, supported by a suitable stand, may be cooled together in a solution of known freezing-

point, as in Hofmeister's method, the time of cooling being one hour. Each tube in succession is then connected by its longer limb with a manometer, and by opening a pinch-cock a pressure equal to 50 mm. of water is caused to act upon the oil. The specification of the Prussian State Railways stipulates that the oil when thus tested after cooling for one hour at a temperature of − 15° C. in winter, or − 5° C. in summer, must flow in the tube at a minimum rate of 10 mm. per minute.

Tagliabue's Standard Oil Freezer (fig. 65), used in the United States, is semicircular in shape, with a flat side. It consists of an inner chamber F, surrounded by an ice-chamber C, with a non-conducting jacket A, filled with asbestos. The oil is contained in a glass cup, 4 inches in depth and 3 inches in diameter, which is fixed upon a rocking shaft by means of which the cup can be tilted and the condition of the oil seen. A thermometer is immersed in the oil, and two others register the temperature of the ice-chamber. Two stopcocks connected to the inner chamber are for the introduction of warm air, if it is desired to raise the temperature, and the tap at the side is for draining away the liquefied ice. A glass window in the flat side enables the oil to be observed.

TABLE XLIX.—FREEZING-POINTS OF SOME VEGETABLE AND ANIMAL OILS.

Oil.	Freezing-points.	
	°F.	°C.
Arachis (earthnut) oil,	+32 to +19·4	0 to − 7
Beech nut oil,	+ 1·4	−17
Cameline oil,	− 0·4	− 18
Castor oil,	+ 14 to − 0·4	− 10 to − 18
Cod-liver oil,	+32 to +14	0 to − 10
Cottonseed oil,	+33·8 to +50	+ 1 to +10
Curcas oil,	+37·4	+ 3
Hempseed oil,	Between +5 and − 17·5	Between − 15 and − 27·5
Lard oil,	+25 to +42	− 4 to − 5·5
Linseed oil,	Between + 5 and − 17·5	Between − 15 and − 27·5
Maize oil,	+14 to − 4	− 10 to − 20
Mustard oil (black),	{ +23 (*Holde*) { + 0·5 (*Chateau*)	{ − 5 (*Holde*) { − 17·5 (*Chateau*)
„ „ (white),	+17·6 to +3·2	− 8 to − 16
Neatsfoot oil,	+32 to +50	0 to +10
Nigerseed oil,	Below +15·8	Below − 9
Olive oil,	+39·2 to +21·2	+ 4 to − 6
Poppyseed oil,	+ 3·2 to − 1·3	− 16 to − 18·5
Porpoise oil,	+ 3·2	− 16
Rape oil,	+28·4 to +10·4	− 2 to − 12
Seal oil,	+28·4 to +26·6	− 2 to − 3
Sesamé oil,	+24·8 to +21·2	− 4 to − 6
Sperm oil (Southern and Arctic),	About 32°	About 0°
Sunflower oil,	+3·2 to − 1·3	− 16 to − 18·5
Walnut oil,	Between +5 and − 17·5	Between − 15 and − 27·5

TABLE L.—FREEZING-POINTS OF MINERAL LUBRICATING OILS.

Description.	Freezing-point.
Scotch oils, .	About 32° F. (*Veitch Wilson*).
American oils,	Very variable. Depends largely upon the amount of solid hydrocarbons present. Winter machinery oil generally sets at 25° to 32° F. (– 4° to 0° C.) by Archbutt's method ; but oils which remain fluid at 0° to 10° F. (– 18° to – 12° C.) are met with.
Russian oils, .	The best qualities of refined machine oil do not cease to flow when cooled to zero Fahr. (– 18° C.).

F.—MELTING-POINTS OF FATS AND LUBRICATING GREASES.

Melting and Solidifying Points of Fatty Acids.—In the melting of natural fats, mixed fatty acids, lubricating greases, etc., the same phenomena present themselves as are observed in the setting or solidifying of oils, viz. :—that, as we are dealing with mixtures, the temperature of incipient fusion, at which some portion of the substance becomes fluid, and the temperature of complete fusion, at which the whole has liquefied, are not, as a rule, the same. It has also been observed that the melting-points of fats and fatty acids may be profoundly modified by previous heating of the melted substance. Thus, Clague [1] found that the melting-point of cacao-butter, originally 75° F., was raised to 86° F. by keeping the melted fat at a temperature just under 100° F. for two hours. A temporary change in the melting-point usually occurs immediately after the substance has been melted and re-solidified. Thus Bevan [2] found that a crystallized fat obtained from lard, which had been melted in a test-tube and then caused to solidify rapidly by chilling in cold water, re-melted at a temperature about 15° below the first melting-point ; on gradually raising the temperature, the fat re-solidified and regained its normal melting-point. In consequence of such facts as the above, the temperatures recorded as the melting-points of fats and fatty acids by different observers, using different methods of preparation and manipulation, unfortunately present discrepancies which will not be removed until some uniform system of testing has been agreed upon.

In the examination of lubricants, the object of a melting-point determination may be twofold. Firstly, a knowledge of the melting-point of a fat or lubricating grease may be required for the purpose of ascertaining its behaviour under the practical conditions of lubrication ; and secondly, the melting- or solidifying-point of a fatty acid

[1] Allen, *Coml. Org. Anal.*, vol. iii. pt. ii. p. 570.
[2] *Analyst,* xviii. (1893), p. 286

or of a mixture of fatty acids may be required as a means of identifying the oil or fat from which the fatty acid or mixture has been obtained.

Preparation of the Substance.—Whatever method be employed, certain precautions must be observed in the preparation of the substance, chief of which are the following :—

(1) Except in the case of lubricating greases ('solidified oils') every trace of moisture present must be removed. Having melted the substance in the water-oven and allowed all visible water to settle out, the fat or oil is poured off, and the remaining traces of moisture are got rid of either by filtering through dry filter paper or by further heating in the water-oven until a cold glass placed over the beaker no longer becomes dimmed by condensed water vapour. Lubricating greases, in which water may be present as an essential constituent, must, of course, be tested without any previous preparation.

(2) In melting fats or fatty acids, previous to the determination of the melting-point, the temperature should not be raised higher, and the heating should not be continued longer, than is absolutely necessary.

(3) Sudden chilling to hasten re-solidification must not be resorted to. The substance must be allowed to solidify naturally. If the temperature of the room be above the solidifying-point, the substance should be placed in a sufficiently cool cupboard or refrigerator, and after solidification has taken place, at least an hour or two, and in most cases from twelve to twenty-four hours, should be allowed to elapse before the determination of the melting-point is undertaken.

Determination of Melting- and Solidifying-points.—Pohl's Method.—By this method the temperature of incipient fusion, at which a substance begins to melt, is determined. The bulb of a thermometer T (fig. 66) is dipped into the melted substance and removed with a coating of the substance adhering to it. After this has solidified, and has remained for a sufficient length of time to acquire its normal melting-point, the thermometer is fixed, by means of a cork, in a long boiling-tube C, the bulb of the thermon eter being placed about ½ inch above the bottom of the tube. A groove is cut in the side of the cork for the escape of air. The tube is then supported in the clamp of a retort stand, about 1 inch above a disc of sheet iron or asbestos, which is heated by means of a small flame so that the temperature rises very gradually. The moment a drop of liquefied fat is observed to collect at the lower part of the thermometer bulb, the temperature is read off and is recorded as the melting-point. This is a very good method for the examination of tallow and other fats.

Stock's Method for Greases.—The following modification of Pohl's method has been recommended by Stock for ascertaining the melting-points of soap-thickened oils.[1] A clean, narrow test-tube is fitted over the lower end of a thermometer, by means of a band of stout indiarubber-tubing, the annular space b tween the walls of the tube and the thermometer not exceeding one-sixteenth of an inch. The narrow test-tube is fixed, by means of a cork, within a wider and longer tube. A small quantity of the sample to be tested is taken upon the bulb of the thermometer, which is then carefully inserted into the inner tube, down to within half an inch of the bottom. The wider tube is then immersed in a beaker of either water or clear lard oil (according to the melting-point of the grease) and is heated on a disc of asbestos millboard supported over an Argand-Bunsen. By bringing the tube up to the side of the beaker, the temperature at which the mass flows

[1] *Analyst*, xiv. (1889), p. 2.

down to a clear bead at the bottom of the tube may be observed, by means of a hand-lens if necessary. This is recorded as the melting-point of the sample.

Capillary Tube Method.—This simple method for determining the point of incipient fusion is frequently used for the examination of fatty acids and other substances of fairly definite, and not too low, melting-point. There are several ways of operating, but the following is one of the most convenient. The capillary tubes, which are made by drawing out soft glass tubing, should be very thin-walled, about 10 cm. long and 1 mm. in internal diameter. They are left open at both ends. One end is dipped into the
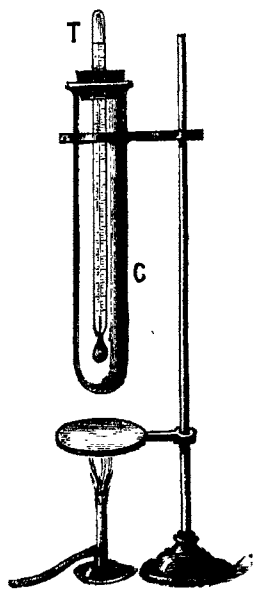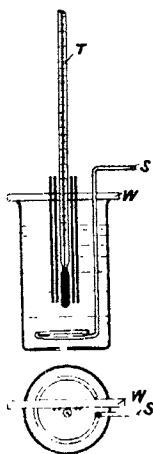
FIG. 66.   FIG. 67.

melted substance, until enough has risen to fill about 1 centimetre of the tube, which is then laid aside in a cool place for several hours, preferably over night, for the substance to solidify and regain its normal melting-point. The other end of the tube is then held for a moment in a small flame and, while hot, is pressed against a small bar of wood W, fig. 67, coated with sealing-wax, by which means four or more of such tubes may be supported in a beaker of water as shown in the sketch. The beaker is placed upon a disc of asbestos millboard over a burner, and a thermometer T, held by a clamp or suspended by a cord, is placed with its bulb close to the filled ends of the capillary tubes. The water in the beaker is then slowly warmed up and continually stirred by the glass stirrer S, and the temperatures at which the substances melt and rise up the capillary tubes are recorded. The mean of two experiments in separate tubes, which should closely agree, is taken as the melting-point of the

substance. In examining mixed fatty acids, it is frequently noticed that a portion will liquefy and run up the tube, leaving the remainder still solid behind. Clague found that the melting-point of cacao-butter determined in a capillary tube varied according to the diameter of the tube.

Bensemann's Method,[1] which is preferable to the above, determines two points, viz.—the temperature of incipient fusion and the temperature of complete fusion. A piece of narrow thin-walled tubing is drawn out to a capillary point and sealed at the small end. A small portion of the substance is then melted in the wider portion of the tube, in the position shown at A a (fig. 68), and is allowed to solidify. After a sufficient interval the tube is attached, by means of two small indiarubber rings cut off a piece of tubing, to a thermometer, with the fat close to the bulb, and the thermometer is supported vertically in a beaker of water. The water is
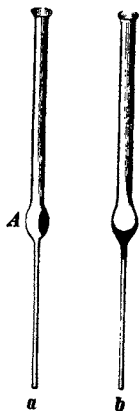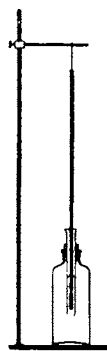
FIG. 68. FIG. 69.

slowly warmed up, with continual stirring, until some of the fat begins to flow; the temperature observed at this moment is the '*point of incipient fusion.*' When the substance has melted to a perfectly clear and transparent liquid as shown at b (fig. 68), the temperature is again read off and is the '*point of complete fusion.*'

Bach's Method.—Bach and Hubi have published a number of melting- and solidifying-points of fatty acids which were ascertained in the following way. The substance was brought into a test-tube about 7 mm. in diameter, and whilst being stirred gently with a thermometer, the temperature was noted at which the mass became quite clear ('*melting-point*'), and that at which a cloudiness began to form ('*solidifying point*').

Cook's Method.[2]—This is a modification of T. Redwood's method.[3] Two beakers are supported one within the other, the minimum space between them being 1 inch at the sides and 1½ inches at the bottom. About 1 inch in depth of mercury is placed in the inner beaker. The outer beaker contains either water or melted paraffin (according to the temperature required), the surface

[1] *Jour. Soc. Chem. Ind.,* iv. (1885), p. 535.
[2] *Proc. Chem. Soc.,* xiii. (1897), p. 74.
[3] *Analyst,* i. (1877), p. 51.

of which must be at least 3 inches above the surface of the mercury. Minute fragments of the substance whose melting-point it is desired to determine are placed on a small piece of ferrotype-plate (with the varnish removed), or on a microscope cover-glass, and floated on the surface of the mercury, in which the bulb of a thermometer is immersed. The beaker is covered with a card. The water or paraffin in the outer beaker is then slowly heated up with frequent stirring, until the substance is observed to melt; it is then allowed to cool, and the solidifying-point may be read off. This method is said to give closely concordant results.

TABLE LI.—MELTING-POINTS OF SOME FATS, WAXES, ETC.

Description.	Name.	Melting-points.	
		° F.	° C.
Fats.	Japan wax,	122·7–132·8	50·4– 56
	Coconut oil,	68·0– 82·4	20 – 28
	Palm nut-oil,	73·4– 86·0	23 – 30
	Palm oil,	80·6–108·5	27 – 42·5
	Cottonseed stearin,	78·8–104	26 – 40
	Tallow (mutton),	111·2–123·8	44 51
	„ (beef),	107·6–119·3	42 – 48·5
	Bone fat,	69·8– 71·6	21 – 22
	Lard.	96·8–118·4	36 – 48
	Horse fat,	107·6–109·4	42 – 43
Waxes.	Wool fat (neutral),	87·8–108 5	31 – 42·5
	Spermaceti,	109·4–113	43 – 45
	Beeswax,	142·7–158	61·5– 70
	Carnauba wax,	181·4–186·8	83 – 86
Hydrocarbons.	Vaseline	104–122	40 – 50
	Paraffin wax	98–137	36·7– 58·3
	Cerasin (refined ozokerite),	141·8 172 4	61 – 78

Dalican's 'Titre Test.'—This test, which was devised by Dalican for the valuation of tallow by determining the solidifying-point of the mixed fatty acids, has been applied by Lewkowitsch to a large number of oils and fats The fatty acids, obtained from 100 grms. of fat by the method described on p. 237, perfectly dried by filtration through paper in the water-oven and allowed to solidify over night, are re-melted at as low a temperature as possible and introduced into a stout-walled test-tube, measuring 7 inches long by 1½ inches diameter, which is filled rather more than half-full. The tube is supported, by means of a cork or a rubber ring, in a wide-mouthed bottle of colourless glass (see fig. 69), and a Centigrade thermometer, grad uated, say from 0° to 70°, in fifths of a degree, is suspended with its bulb in the centre of the fatty acids. As soon as crystals begin to appear at the bottom of the tube, the fatty acids are stirred by giving the thermometer a rotatory movement, first thrice to the right, then thrice to the left, and then continuously in one direction, without touching the sides of the tube, but

TABLE LII.—MELTING- AND SOLIDIFYING-POINTS OF SOME MIXED FATTY ACIDS.

| Class. | Mixed Fatty Acids from | Melting-points °C. | | | Solidifying-points °C. | |
| | | Bensemann's Method. | | Other Methods. | Various Methods. | 'Titre' Tests (Lewkowitsch). |
		Point of Incipient Fusion.	Point of Complete Fusion.			
Vegetable Non-drying Oils and Fats.	Olive oil,	23-24	26-27	{ 24-27* / 19-28·5† }	} 17-24·6	17·15-26·4 (12 samples)
	Hazel nut oil,	..	.	17-25	9-20	
	Ben oil,	..	.	..	.	37·2-37·8
	Arachis (earthnut) oil,	31-32	34-35	27-33	22 31	29·2
	Castor oil,	..	..	13	2-3	
	Japan wax,	..	..	56-57	53 56·5	59·4
	Coconut oil,	..	..	24-27	15·7-20·4	22·5-25·2
	Palm nut oil,	..	..	20·7-28·5	.	20·5-25·5
	Palm oil,	..	..	41-50	39-46·2	35·9-45·5
	Cottonseed stearin,	.	..	27-30	21-23	35·1
Vegetable Semi-drying Oils.	Rape oil,	18-19	21-22	16-21	10·5-18·5	12·2-13·6
	Rape oil (Stettin),	..	..	..	..	18·5‡
	Ravison oil,	..	..	..	..	Below 0°‡
	Mustard oil,	.	..	15-17	15·5	
	Curcas oil,	.	..	27·5	.	28·6
	Cottonseed oil,	39-40	42-43	34 40	30·5-36	37·6
	Cottonseed oil,	..	..	.	..	32·7-35·2 (part of the stearin removed)
	Sesamé oil,	25-26	29-30	21-32	18·5-28·5	22·9-23·8
	Beech nut oil,	..	..	23-24	17	..
	Maize oil,	..	..	18-20	14-16	..
	Cameline oil,	..	..	18-20	13-14	..
Vegetable Drying Oils.	Linseed oil,	..	.	below 13 24	13·3-17·5	19·4-20·6
	Hempseed oil,	..	..	17-19	14-16	16·6
	Poppyseed oil,	..	.	19-22	15·4-17	16·2
	Walnut oil,	..	.	15-20	16	..
	Nigerseed oil,	..	.	25-26·6	..	..
	Sunflower oil,	..	..	17-24	17-18	..
Animal Oils and Fats.	Neatsfoot oil,	..	.	29·8-30·8	..	26·5
	Tallow (mutton),	49-50	53-54	46-49	..	41·5-48·3
	" (beef),	42-44	45-47	45	..	38·3-46·3
	Bone fat,	.	.	30	28	
	Horse fat,	.	.	37·5-39·5	37·3-37·7	33·7
	Lard,	43-44	46-47	35-44	32·5-39	42·0
Marine Animal Oils and Fluid Wax.	Sperm oil (inc. Arctic),	..	.	10·3-13·3	..	8·6-11·9
	Whale oil,	.	..	14-18§	..	23·9
	Seal oil,	..	..	22-33	..	15·9
	Cod-liver oil,	..	..	..	..	13·9-24·3
	Sardine oil,	.:	..	..	..	27·6-28·2
Wax (solid)	Wool fat,	..	..	52·6‡	..	..

* 208 samples by De Negri and Fabris.
† All observers; the lower number obtained with Californian oils.
‡ Archbutt.
§ 27° Jean.

taking care that the whole mass is kept uniformly mixed. When the mixture becomes turbid throughout, the mercury is watched closely. At first it will fall slowly, but at a certain point it will rise a few tenths of a degree, sometimes 2 or 3 degrees, and will then remain stationary for a short time before commencing to fall again. The point at which it remains stationary is the '*titre*' or solidifying-point of the fatty acids. Freundlich states (*Analyst*, 1900, p. 105) that the temperature to which the thermometer finally rises is partly dependent upon that to which it was made to fall during the stirring of the fat, and that to ensure concordant results too prolonged stirring must be avoided in making this test.

G.—REFRACTIVE INDEX.

In the analysis of lubricating oils, the refractometer will be found a useful though not an indispensable instrument. The kind of instrument employed may be one such as Abbe's, by which the index of refraction of the oil is measured, or a differential refractometer, such as that of Trannin or Amagat and Jean, in which the deviation of the ray is measured on an arbitrary scale.

The following table contains the refractive indices for the D line of some oils as determined by Abbe, Strohmer, Holde and others with Abbe's refractometer :—

TABLE LIII.—REFRACTIVE INDICES.

Oils, in order of their Refractive Indices.	Index of Refraction	
	at 15° C.	at 20° C.
Neatsfoot oil,	1·467 –1·471	...
Olive oil,	1·4670-1·4717	1·4690
Sperm oil,	...	1·470
Rape oil,	1·4720–1·4757	1·472–1·475
Cottonseed oil,	1·4743–1·4752	1·4748
Sesamé oil,	1·4748–1·4762	...
Mustard oil,	1·4751–1·4760	...
Poppy oil,	1·478	...
Castor oil,	1·4795–1·4803	1·490
Walnut oil,	1·4804	1·491
Cod-liver oil,	1·4800–1·4852	1·4800
Whale oil,	...	1·483
Linseed oil,	1·4835	1·4780
Beechnut oil,	...	1·5000
Mineral lubricating oil,	1·490 - 1·500	...
Rosin oil,	1·530 –1·550	...

The instrument generally employed for commercial purposes is the **Oleo-refractometer** of Amagat and Jean, the essential parts of which are shown in section in fig. 70 (p. 208). It consists of a collimator and a telescope

TABLE LIV.—TESTS OF OILS WITH AMAGAT AND JEAN'S
OLEO-REFRACTOMETER.

Class.	Name of Oil, etc.	Refractometer. Degrees at 22° C.
Vegetable Non-drying Oils.	Olive oil, ...	±0 to +3·5
	Arachis (earthnut) oil, . .	+3·5 to + 7
	Castor oil, ...	+39 to +46
Vegetable Semi-drying Oils.	Rape oil, ...	+15 to +20
	Ravison oil, ...	+18 to +25
	Cottonseed oil, ...	+17 to +23
	Sesamé oil, ...	+13 to +18
	Beechnut oil, ...	+16·5 and +18
	Cameline oil, ...	+32
Vegetable Drying Oils.	Linseed oil, ...	+48 to +54
	Hempseed oil, ...	+32 to +37·5
	Poppyseed oil, ...	+23·5 to +35
	Walnut oil, ...	+35 to +36
	Nigerseed oil, ...	+26 to +30
	Sunflower oil, ...	+35
Animal Oils and Fats.	Neatsfoot oil, ...	−1 to −4
	Sheep's foot oil, . . .	±0
	Lard oil, ...	±0 to +5·5
	Tallow oil, ...	− 1 to − 5 (−15 ?)
	Tallow, ...	−15 to −18 (−40 ?)
	Lard, ...	− 8 to −14
Marine Animal Oils	Sperm oil (inc. Arctic), .	−13 to −17·5
	Whale oil, ...	+30·5 to +48
	Seal oil, ...	(+8 ?)+30 to +36
	Cod-liver oil, ...	+38 to +53
	Shark liver oil, . . .	+29 to +35
	Sardine oil, ...	+50 to +53 *
Miscellaneous.	Rosin oil	+78

* At 45° C.

having a common axis, between which is fixed a hollow prism for containing the oil.   The hollow prism, A, is a metallic cell having opposite glass windows, CC, fixed at an angle of 107°, and surrounded by a bath of sheep's foot oil ('huile type') contained in the vessel BB, which is furnished with opposite parallel windows, DD¹.   The temperature of the oils in the cell B and in the prism are kept at a constant temperature of 22° C. by means of an outer water-bath not shown in the figure.   The light rays from an ordinary gas flame placed at the end of the collimator G traverse the oils, and are focussed by the lens E¹ of the telescope upon the photographed scale H, and viewed through the magnifier M.   The collimator has, instead of a slit, a movable shutter with a sharp vertical edge, which throws part of the field into shadow, and the edge of this shadow is focussed sharply upon the scale.

In using the instrument, the prism, A, is first of all filled with some of the standard (sheep's foot) oil, similar to that contained in the outer cell : there is then no refraction, and the edge of the shadow if not exactly on the zero of the scale is adjusted to it by moving the shutter.   The standard oil having been drawn off through the tap R, and the prism rinsed with ether and dried, the oil to be tested is introduced, having been previously brought
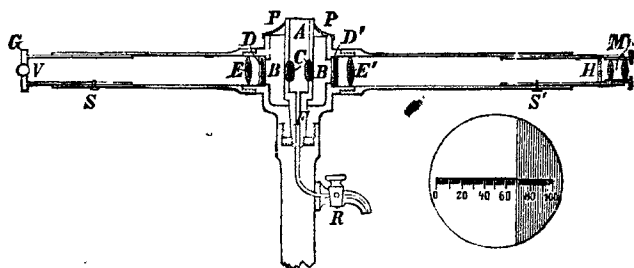
FIG. 70.

to exactly 22° C. in temperature.   The deviation is then read off upon the scale.

The results obtained by different instruments of this kind are only comparable if the angle of the prism of each instrument, the focal distance o the lens E¹, and the scale H are precisely the same.   Allen states that thi is not always the case, and that a sample of oil which showed 4·5° in⁴ hi instrument gave 6° and 11°, respectively, in two others.   Therefore, ever: new instrument before being purchased should be tested with genuin samples of two or three typical oils, say olive, linseed, and castor, and th deviations compared with the numbers given in Table LIV., which contain the results of various observers.

H.—COLOUR AND APPEARANCE.

The *colour* and *appearance* of lubricating oils are very variable Some, like lard oil, are almost colourless, but most present a variet: of shades of yellow, red, brown and green.   All the fixed oils an

the refined mineral oils are transparent; the unrefined natural and reduced mineral oils are mostly opaque.   Some exhibit fluorescence.

As the colour and appearance of oils depend upon the conditions under which they are viewed, this physical character, when of importance, must be observed under definite conditions.   Redwood uses for the purpose Lovibond's tintometer, observing the colour of the oil in a 2-inch cell.[1]   For the darker oils, a $\frac{1}{4}$-inch cell is convenient.

[1] *Jour. Soc. Chem. Ind.*, ix. (1890), p. 14.

CHAPTER VII.

A.—FREE ACID OR ACIDITY.

I. **Nature and Amount of the Free Acid in Oils.**—Free acid in an oil or fat may consist of

(1) *Free fatty acid*, naturally existing in small quantity in most vegetable oils, or set free in larger quantity by the decomposition of a vegetable or animal oil during storage in a crude state, or by the action of sulphuric acid in the refining process;

(2) *Rosin acids*, present as a natural constituent of rosin oil, or as added rosin;

(3) *Organic (petroleum) acids*, naturally existing in crude mineral oil;

(4) *Free sulphuric or other mineral acid* used in refining the oil and not properly washed out.

Free acid of any kind is objectionable in a lubricant for metallic surfaces, owing to its corrosive action. Free fatty acids have the additional disadvantage that the soaps formed by their action on metals dissolve in the oil and cause it to thicken and gum.

Mineral lubricating oils in the dark unrefined state contain small quantities of weak organic acids varying, according to Holde,[1] from 0·2 to 2·0 per cent., calculated as oleic acid; but the pale oils, when well refined, are almost perfectly neutral. Owing to their constitution, mineral oils are not capable, like animal and vegetable oils, of developing acidity by decomposition, though some of the contained hydrocarbons can undergo oxidation with formation of resinous and asphaltic products. Acidity of refined mineral oils is most likely to be due to the accidental presence of sulphuric acid, which is used in refining, but such an impurity is now rarely met with and would show great carelessness in washing the oil.

All vegetable and animal oils, on the other hand, contain free fatty

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[1] *Die Untersuchung der Schmiermittel.*

acids in proportions varying from less than 0·5 per cent. to· upwards
of 50 per cent. The least acid oils are those refined with alkali, such
as '*animal oil*' and *cottonseed oil*; the acidity of these oils varies,
according to the authors' experience, from 0·08 to 0·26 per cent, *i.e.*
it is practically negligible. More acidity is met with in those oils
which are refined with sulphuric acid, such as *rape oil*, which contains
on an average about 2·2 per cent. of free (oleic) acid, varying from
·1 per cent. to about 6 per cent., but seldom exceeding 5 per cent.
378 samples of *refined rape oil* tested by Archbutt during three
years ending 31st March 1905, all representing large contracts, gave
the following results :—

Number of Samples.					Free (Oleic) Acid, per cent.
122	.	.	.	.	1·1–1·9
223		.	.	.	2·0–2·9
30	.		.	.	3·0–3·9
3	.		.	.	·0–5·7
378		(*Average*),			2·21 per cent.

Traces of free sulphuric acid are met with in rape oil which has
been refined with this acid (see p. 313).

Those oils which are stored in a crude state, and are not afterwards
chemically refined, often contain such large amounts of free fatty
acids as to quite unfit them for use as lubricants.

Thus, in 9 samples of *palm oil*, Archbutt found from 11·9 to 78·9
per cent. of free (palmitic) acid.[1] Lewkowitsch states that he has
found from 50 to 70 per cent. of free (palmitic) acid in a large number
of commercial palm oils.

In 151 samples of *olive oil* from various sources, Archbutt found
the following percentages of free (oleic) acid [2] :—

TABLE LV.

Number of Samples.	Source.	Free (Oleic) Acid per cent.		
		Highest.	Lowest.	Average.
70	Spain, . . .	25·1	1·5	5·5
36	Italy, . . .	25·2	0·9	8·5
28	Sicily, . . .	16·6	0·5	·1
12	Candia, . . .	16·8	5·5	9·5
3	Levant, . . .	13·5	8·5	10·4
2	Zante, . . .	8·7	4·8	6·7

[1] *Analyst*, ix. (1884), p. 171.
[2] *Jour. Soc. Chem. Ind.*, viii. (1889), p. 685.

136 samples of olive oil, supplied under contract to a specification limiting the free (oleic) acid to a maximum of 4·0 per cent., contained a minimum of 0·6 per cent., a maximum of 7·4 per cent., and an average of 2·85 per cent. of free (oleic) acid.

Other observers have found from 1·0 to 27·2 per cent. of free (oleic) acid in olive oils.

In 25 samples of *tallow* examined by Deering [1] the following percentages of free (oleic) acid were found :—

TABLE LVI.

Number of Samples.	Source.	Free (Oleic) Acid per cent.		
		Highest.	Lowest.	Average.
13	Russian, ...	12·20	2·20	5·48
4	Australian beef, . .	8·85	1·75	4·47
1	„ mutton, . .	7·15	0·85	3·91
2	Town tallow, . . .	6·95	4·55	5·75
1	Unknown, ...	2·10	...	...
1	Town tallow, six years old,	25·0	...	...

Eighty-eight samples of *tallow* examined by Archbutt gave the following results :—

TABLE LVII.

Number of Samples.	Source.	Free (Oleic) Acid per cent.		
		Highest.	Lowest.	Average.
55	Home melted, . . .	11·90	1·40	4·89
9	Australian mutton, . .	12·84	1·00	4·84
11	South American beef, .	7·60	0·70	2·07
12	Unknown, ...	10·60	1·30	4·65
1	„ . . .	83·60	...	...°

227 samples of tallow, supplied to a specification limiting the free oleic) acid to 4·0 per cent., contained a minimum of 0·5 per cent., maximum of 26·2 per cent., and an average of 2·86 per cent., of ree (oleic) acid.

In 23 samples of *Indian castor oil* examined by Deering and ledwood,[2] the acidity, calculated as oleic acid, ranged from 0·70 to ·30 per cent., and averaged 2·58 per cent.; 6 samples of castor oil

[1] *Jour. Soc. Chem Ind.*, iii. (1884), p. 540.
[2] *Ibid.*, xiii. (1894), p. 961.

for lubricating, examined by Archbutt, contained from 1·47 to 2·70 per cent. ; and Thomson and Ballantyne found, in two samples, 1·46 and 2·16 per cent., respectively.   But Nordlinger found[1] in 9 samples of expressed castor oil from 0·62 to 18·61 per cent. of free acid, or an average of 9·28 per cent. ; whilst in 5 samples of extracted oil he found from 1·18 to 5·52 per cent., or an average of 2·78 per cent.

In 8 samples of *sperm oil*, seven examined by Deering and one by Thomson and Ballantyne, the acidity as oleic acid ranged from 0·55 to 2·64 per cent., and averaged 1·7 per cent. ; in two samples of *Arctic sperm oil* it was 1·97 and 2·11 per cent. respectively, averaging 2·04 per cent.   Fourteen samples of *Southern sperm oil*, examined by Veitch Wilson,[2] contained from 0·5 to 2·0 per cent. of acidity, averaging 1·32 per cent. ; and 29 samples of Arctic sperm oil contained from 0·5 to 3·0 per cent. of acidity, averaging 1·78 per cent.   Therefore, Arctic sperm oil is a little, but not much, more acid than Southern sperm oil.

Acidity is not the same as *rancidity*.   Ballantyne[3] has shown that oils can become rancid without the liberation of any free acid whatever, and the converse is also true.   The researches of Ritsert and others have proved that the changes which produce rancidity of oils are due to oxidation.[4]

The acidity of most fatty oils tends to increase by keeping, but *refined* oils can be kept for considerable periods without undergoing any change of practical importance.   Thus, Ballantyne[3] found that olive, rape, castor, and arachis (ground nut) oils remained unchanged in acidity for six months, whether kept in the dark in corked bottles or exposed freely to sunlight and air ; and some neutral palm oil prepared by one of the authors, after being kept in a stoppered bottle in a dark cupboard for fourteen years, was found to contain only 0·4 per cent. of acidity, calculated as palmitic acid, all of which may have been originally present, as the acidity was not determined after the oil had been purified.

II. **Effects of Free Fatty Acids in Lubricants.**—Burstyn,[5] who was one of the first to pay attention to the corrosive effects of fatty oils upon axles and bearings, showed, in 1876, that the action of olive oil on brass was greater the more acid the oil.   It is, therefore, to be regretted that Redwood[6] and others who have been at much pains in investigating the relative action of various fatty oils upon metals did not determine the amount of free acid contained in the oils they experimented with.   This omission makes their experiments almost valueless, as the different effects observed may have been entirely

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[1] *Zeits. Anal. Chem.*, xxviii. 183.
[2] Carpenter and Leask, *Soap, Candles, Lubricants, and Glycerin*, p. 298.
[3] *Jour. Soc. Chem. Ind.*, x. (1891), p. 29.
[4] For a full discussion of the subject see Lewkowitsch, *Analysis of Oils, etc.*, vol. i. p. 19 *et seq.*
[5] *Dingler's Polyt. Journal*, ccxvii. p. 314.
[6] I. J. Redwood, *Jour. Soc. Chem. Ind.*, v. (1886), p. 362.

due to differences in the acidity of the various oils, and not to any difference in the properties of the oils themselves.

Not only is it probable that neutral fatty oils have no chemical action on metals, but it is doubtful whether even free fatty acid can exert much action in the absence of air and moisture. Thus Fox [1] suspended thin strips of lead in the mixed fatty acids prepared from olive and linseed oils, and found that after having been heated for several days to 220° F. the lead had not lost weight. E. Donath [2] took bright, accurately weighed strips of iron, copper, brass, and zinc, and completely immersed some in strongly acid olive oil and others in crude oleic acid. At the end of three weeks the strips were found to have suffered very little loss of brightness and a scarcely perceptible loss of weight. Even when the oils were kept heated to 70°–80° C. (158°–176° F.) for several days, the metals were not attacked. But if, previous to immersing the metals in the acid oils, the latter were thoroughly emulsified with air, or especially with water, by vigorous shaking, corrosion readily took place. Donath concluded from these experiments that the corrosive action on metals of lubricating oils containing free fatty acids depends to a great extent upon whether the oiled surfaces come into contact with atmospheric oxygen, and whether, by condensation or other means, water gets into the oil. It is difficult to account in any other way for the very erratic manner in which corrosion sometimes takes place, such as is illustrated by the following experiment made by one of the authors several years ago.

Four samples of *railway wagon grease*, each composed, in the same proportions, of tallow, palm oil, soap, and water, but containing respectively 0·4, 1·4, 1·6, and 4·0 per cent. of free fatty acid, were taken, also a sample of very acid palm oil, free from water, containing 72·2 per cent. of free (palmitic) acid. Into each of these five specimens of grease, etc., two strips of bright steel were inserted, and after an interval of four months they were taken out, cleaned and examined, with the following results : —

Strips immersed in	Free Fatty Acid per cent.	Condition of the Steel after Four Months' immersion.
Grease No. 1,	0·4	Both strips bright.
Grease No. 2,	1·4	„ „
Grease No. 3,	1·6	1 strip bright, 1 deeply corroded in one spot.
Grease No. 4,	4·0	Both strips deeply corroded on one side.
Acid palm oil,	72·2	Both strips merely stained and not corroded.

If fatty acids alone can attack steel, the two strips immersed in the very acid palm oil should have been the most corroded, instead

[1] *Analyst*, viii. (1883), p. 116.
[2] *Dingler's Polyt. Journal*, ccxciv. p. 186 ; *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 282

of which they were merely stained, whilst the strips immersed in the grease containing only 4 per cent. of free fatty acid were both deeply corroded, doubtless because of the simultaneous presence of water. It will be observed that the most acid grease proved to be the most corrosive of the four.

Oleic acid, water, and iron filings, if heated together in a test-tube, react briskly, hydrogen being evolved and brown oleate of iron formed. This compound is decomposed, by oxidation, into ferric oxide and free oleic acid, which again attacks more iron; in this way a comparatively small quantity of the free fatty acid has been known to perforate wrought-iron plate more than $\frac{1}{2}$ inch in thickness.[1]

Although a metal in stationary contact with a cold solid grease containing free fatty acid and water may undergo serious *local* pitting, as proved by the above experiments, the corrosive action upon a brass or journal of the free fatty acid existing in a fluid oil, or in a grease lubricating a journal in motion, may escape notice, because it is spread over the whole of the rubbing surfaces.   But the effect of chemical action will be observable in the thickening of the oil and in the formation of gummy deposits. Thus, a mixture of olive oil with from 10 to 15 per cent. of mineral oil, which had been taken out of a railway carriage axle-box after about three weeks' use, was found to be much thickened, of a deep green colour, and contained in solution much copper and zinc. Some of the oil was dissolved in ether and shaken with dilute nitric acid to extract the dissolved metals; the ether was then evaporated, and the oil was recovered with its original colour and almost its original fluidity restored. From this it is evident that the thickening and gumming of fatty oils on bearings, generally attributed solely to oxidation, may be due partly to soaps formed by the chemical action of the free fatty acids upon the metal of the bearing, dissolving in and thickening the oil. In the oil used by woolcombers for oiling wool, the amount of free fatty acid is of secondary importance compared with freedom from a tendency to oxidize and form a sticky residue on the wool fibre.[2]

III. **Determination of Acidity.**—The acidity of lubricating oil, which, as already stated, may be due to the presence of more than one description of free fatty or resin acid, or (rarely) to a mineral acid, is generally determined volumetrically and expressed either as oleic acid or as sulphuric acid or sulphuric anhydride. In this country it is usual to express the acidity of a fixed oil or fat in terms of oleic acid ; on the Continent the acidity is frequently stated as sulphuric anhydride.   Another method of expression, adopted by Benedikt, is known as the '*acid value*,' which is the *number of milligrammes of potash* (KOH) *required to neutralize the free acid in 1 grm. of oil.* Koettstorfer has proposed to express the acidity in *degrees*,' which

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[1] V. Wartha, *Dingler's Polyt. Journal*, ccxv. p. 115 ; Stock, *Chem. News*, xxxix. (1879), p. 6.
[2] Richardson and Jaffé, *Jour. Soc. Chem. Ind.*, 1905, 534.

are the *number of c.c. of normal alkali required to neutralize the acidity of 100 grms. of oil.* Koettstorfer's degrees have the advantage to a chemist that they are at once converted into any required acid, if multiplied by the saponification equivalent of that acid ÷ 1000. The relation of the different methods of expression is shown in the following table by Benedikt :—

Degrees ; = c.c. of normal alkali required to neutralize 100 grms. of oil.	Acid Values ; = milligrms. of KOH required to neutralize 1 grm. of oil.	Oleic Acid, per cent.	Sulphuric Anhydride, per cent.
1·0	0·561	0·282	0·040
1·782	1·0	0·5027	0·0713
3·546	1·9863	1·0	0·1418
25·000	14·025	7·05	1·0

For the determination of total acidity, 5–10 grms. of the oil may be completely dissolved in a neutralized mixture of ether (4 parts) and absolute alcohol (1 part) and titrated with an alcoholic decinormal solution of caustic soda, using phenolphthalein as indicator ; or the oil may be merely shaken up in a flask with neutralized methylated spirit (which dissolves the free acid, leaving most of the neutral oil insoluble) and titrated with aqueous caustic soda solution. The latter method is simpler, and is sufficiently accurate ; it is, therefore, preferable for technical purposes. The solutions required are :—

Normal (aqueous) caustic soda solution. 1 c.c. = 0·282 grm. oleic acid. A clear aqueous solution containing 50 grms. of caustic soda in 100 c.c. (see p. 225) is diluted with distilled water free from CO_2, until of correct strength, phenolphthalein being used as indicator in titrating.

Phenolphthalein solution. An alcoholic solution, containing 3 grms. phenolphthalein in 100 c.c., neutralized by shaking with dry precipitated calcium carbonate and filtering.

Neutralized methylated spirit ; prepared by filling a stoppered bottle of about 500 c.c. capacity with ordinary methylated spirit, adding 10 c.c. of phenolphthalein solution, and dropping in normal caustic soda solution from a burette until the liquid assumes a faint permanent pink colour.

To determine the acidity of a fluid oil in terms of oleic acid, weigh 28·2 grms. of the oil into an Erlenmeyer flask of about 250 c.c. capacity, add 50 c.c. of neutralized alcohol and 2 c.c. of phenolphthalein solution. Then add normal caustic soda solution from a burette, cautiously at first, but afterwards in quantities of 0·5 to 1·0 c.c. or more at a time if the crimson colour at first formed disappears quickly on shaking. When the colour begins to disappear slowly, cork the flask and shake it violently, then add the soda in smaller quantities, finally drop by drop, vigorously shaking the corked flask after the addition of each drop, until the alcoholic liquid is

permanently coloured a faint pink. The number of c.c. of normal caustic soda solution used is the percentage of free acid, expressed as oleic acid, in the sample. If the quantity of oil available is small, 2·82 grms. may be titrated with *decinormal* soda, which will give the same result.

A solid fat, such as tallow, may be titrated in the same way as a fluid oil, if the contents of the flask be kept sufficiently heated to maintain the fat in a melted condition. In weighing out the fat, some of it is first melted in a beaker and poured, while melted, into the counterpoised flask until the weight is nearly made up. The flask is then removed from the balance and allowed to become quite cold. It is then replaced, and the exact weight is made up by adding a little more fat. In titrating palm oil, which is sometimes deep red in colour, the half or quarter of 28·2 grms. may be taken and mixed with 100 c.c. of alcohol instead of 50 c.c. ; the colour change can then be sharply detected, even with very red samples. The volume in c.c. is multiplied by 2 or 4, as the case may be, to get the percentage of acid.

Very dark coloured oils, in which the colour change cannot be detected by the above method, should be very well shaken with two or three times their volume of neutralized alcohol, then poured into a separating funnel and left for the liquids to separate. The oil is drawn off into the original flask and shaken again with an equal volume of alcohol, whilst the alcoholic solution in the separator is drawn off into a clean flask. The mixture of alcohol and oil is again poured into the funnel and allowed to separate, the oil is then drawn off and shaken a third time with alcohol. The second and third alcoholic extracts having been mixed with the first, phenolphthalein is added and the liquid is titrated with caustic soda.

Free mineral acid must be tested for separately, as the above methods make no distinction between fatty and mineral acid. To detect the presence of mineral acid, take a known quantity, say 25 c.c., or about the same number of grammes of the oil, and well shake it in a separating funnel with 200 c.c. of hot water. When the water has quite separated from the oil draw it off through a wet filter paper into a flask, and add to the *cold* liquid a few drops of methyl-orange indicator, which is unaffected by fatty acids, but in the presence of free mineral acid will tinge the liquid red. If free mineral acid be detected, the oil may be again shaken several times with small quantities of hot water, until all the acid has been washed out, and the mixed aqueous liquids may then be neutralized by adding normal caustic soda solution until the red colour just changes to yellow. 1 c.c. of normal caustic soda is equivalent to 0·049 grm. of sulphuric acid, or 0·040 grm. of sulphuric anhydride, in the quantity of oil taken. The neutralized solution may be boiled down to a small volume and portions tested with appropriate reagents in order to determine the nature of the acid present. (See also p. 213.)

Oils containing *sulphonated fatty acids* must be well boiled with water by blowing steam through the mixture, in order to decompose the compound acid, thus :--

$$C_{17}H_{34} < \begin{matrix} O.SO_2.OH \\ CO.OH \end{matrix} + H_2O = C_{17}H_{34} < \begin{matrix} OH \\ CO.OH \end{matrix} + SO_2(OH)_2$$

sulpho-stearic acid.   hydroxy-stearic acid. sulphuric acid.
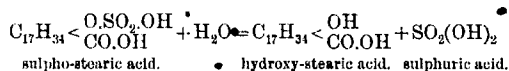
To determine the sulphuric acid, the aqueous liquid, after separation from the greater part of the oil, is evaporated down to about 70 c.c., filtered bright and titrated, cold, with standard soda solution, using methyl orange

as indicator. The liquid may afterwards be acidified, precipitated with barium chloride, and the barium sulphate weighed, if desired.

Gravimetric determination of free fatty and resin acids.—The free fatty and resin acids existing in an oil or fat may be separated and weighed in the following manner :—

5 grms. of the sample are dissolved in ether and rinsed into a separating funnel, into which a few drops of water have been placed to seal the tap. The ethereal solution is shaken repeatedly with small quantities (10 20 c.c. at a time) of a dilute solution of caustic soda (containing 20 c.c. of a 10 per cent. solution of NaOH and 10 c.c. of rectified alcohol made up with water to 100 c.c.) until all fatty acids are extracted (10 c.c. of the dilute soda solution, which is roughly seminormal, will dissolve 1·4 grm. oleic acid). The mixed aqueous extracts are first shaken with a little ether to remove traces of oil, then decomposed with dilute sulphuric acid, and shaken with ether to dissolve the liberated fatty and resin acids. After washing the ethereal solution, it is distilled in a tared flask, and the residue is heated on the water-oven until constant in weight. Resin acids may then be separated and determined by Twitchell's process (p. 238), and, if desired, the neutral oil may be recovered by distilling the original washed ethereal solution.

IV. Amount of Free Acid permissible in Lubricants.—The amount of free acid permissible in a lubricating oil depends upon the nature of the oil and the purpose it is used for. A refined (pale) mineral oil should not contain any acid whatever ; but the dark-coloured 'reduced' oils may be expected to contain traces of weak organic acids varying, according to Holde, from 0·2 to about 2·0 per cent., calculated as oleic acid. Free mineral acid, which can only occur through imperfect refining, should not be permitted in any oil ; but some free fatty acid must be allowed in fixed oils and fats. Experience shows that 4 per cent. of free fatty acid, calculated as oleic acid, is a practicable working limit, and no olive oil, tallow, or other oil containing more than this proportion of acidity should be used for lubricating. The less there is below this amount the better the oil.

'V. Process for refining small quantities of oil.—Neutral oil or tallow required in small quantity for delicate mechanism, instruments, brass taps, etc., can be prepared as follows :—Take a good commercial sample of the oil or fat, containing not more than say 5–7 per cent. of free (oleic) acid, and place it in a bottle with one-third of its volume of caustic soda solution, prepared by mixing a 5 per cent. aqueous solution of caustic soda with half its volume of methylated spirit. Add also some phenolphthalein. Stand the bottle in hot water, so as to raise the temperature of the contents to about 150° F., and then shake the oil and soda together, thoroughly, but not too vigorously. If the crimson colour of the phenolphthalein is bleached, add more soda until the colour remains permanent on continued shaking. Then allow the liquids to separate, while hot, in the bottle or in a separating funnel, and siphon or tap off the lower liquid. Wash the oil by shaking it a few times with a mixture of water two volumes and methylated spirit one volume, allow to stand until the aqueous liquid has separated, filter the oil through a dry filter, and heat it in the water-oven to a temperature not exceeding 212° F. until bright.

B.—DETECTION OF SAPONIFIABLE AND UNSAPONI-FIABLE OIL.

Pure mineral oils and refined rosin oil free from rosin acids are chemically indifferent towards alkalis, but all the fixed oils, fats, and waxes when heated with caustic soda or caustic potash are saponified, with formation of glycerol or wax alcohols and soaps. This difference of behaviour is the basis of the processes for the detection and determination of fixed (saponifiable) oils and hydrocarbon (unsaponifiable) oils in the presence of each other.

I. Detection of Fatty Oil in Mineral Oil.

Lux's test, improved by Ruhemann,[1] depends upon the property possessed by quite small quantities of soap of causing the gelatinization of mineral oil, as well as upon the frothing or foaming of soapy liquids when heated.

3–4 c.c. of the suspected mineral oil are placed in a dry test-tube with a small piece of caustic soda, and the tube is heated in a paraffin bath for fifteen minutes to a temperature of 230° C. in the case of pale coloured oils, or 250° C. in the case of dark mineral oils or cylinder oils. If very small quantities (as small as 2 per cent.) of fatty oil are to be looked for, a duplicate test is made at the same time with metallic sodium instead of caustic soda. On removing the tubes from the bath and allowing them to cool, the presence of a saponifiable oil is indicated by the gelatinization (complete or partial) of the contents of one or both tubes, or by the appearance, on the surface of the oil, of a soapy froth, the amount of which is proportional to the quantity of saponifiable oil present. Both gelatinization and the soapy froth may be observed. Holde states,[2] as the result of a large number of experiments, that by this test as little as 0·5 per cent. of fatty oil may be detected in pale mineral oils, 2 per cent. in dark-coloured oils, and 1 per cent. in cylinder oils.

II. Detection of Mineral Oil in Fatty Oil.

The following test by Holde[2] depends upon the fact that an alcoholic solution of pure soap remains clear on the addition of a limited quantity of water; but, in the presence of mineral oil, the addition of water causes the formation of a turbidity, due to the precipitation of the unsaponified mineral oil.

A piece of caustic potash about the size of a pea, is heated in a test-tube with about 5 c.c. of absolute alcohol until dissolved ; 3 or 4 drops of the suspected oil are then added, and the liquid is boiled for one minute. Or, better still, 5 c.c. of a clear seminormal solution of potash in alcohol (see

[1] *Jour. Soc. Chem. Ind.*, xii. (1893), p. 470.
[2] *Die Untersuchung der Schmiermittel.*

p. 221) are boiled for two minutes with 6 to 8 drops of oil. To the soap
solution thus prepared distilled water is gradually added, well mixing after
each addition, until from 0·5 to 15 c.c. have been added altogether. If un-
saponifiable oil be absent the solution remains clear, even when mixed with
the maximum proportion of water ; but the presence of even 1 per cent.
of mineral oil will cause the formation of a turbidity. Careful observation
s needed, since the characteristic feeble turbidity produced by a very small
proportion of mineral oil (0·5 to 2 per cent.) sometimes disappears again on
the addition of more water, and may, therefore, easily be overlooked. Rosin
oil, if present in smaller proportion than 12 per cent., is not detected   The
higher alcohols formed on saponifying the fluid waxes do not precipitate at
once on adding water, but remain dissolved in the soap solution for some
considerable time ; therefore, this test can be used for the detection of
mineral oil in sperm oil (*Lobry de Bruyn* [1]).

C.—THE SAPONIFICATION VALUE.

1.—Meaning and Use of this Value.

The reactions between caustic alkalis and the esters contained in
oils and fats take place in definite proportions, and in the case of
any single ester can be represented by an equation (see p. 105).
Thus, one molecule of every glyceride requires for saponification
three molecules of potash, whilst one molecule of the ester of a
monohydric alcohol requires one molecule of potash. The quantity
of potash required for the saponification of any single ester, such as
pure stearin or olein, can therefore be calculated, and serves to
identify it, but the quantity required to saponify the mixed esters
known as · fixed oils, fats, and waxes can only be ascertained by
experiment, and when expressed as a percentage [2] is called the
saponification value' of the oil, fat, or wax.

Reference to the table on p. 222 will show that the majority of
saponifiable oils require about the same percentage of potash for
saponification, the exceptions being rape oil, mustard oil, castor oil,
and some of the fish oils, which require less than the average, and
butter fat, palm nut oil, coconut oil, and porpoise and dolphin jaw
oils, which require considerably more. The waxes have character-
istically low saponification values. Hydrocarbon oils, of course, have
none. Hence, a knowledge of the saponification value enables us to
detect, and frequently to approximately determine, the proportion of
hydrocarbon oil in a mixture, to identify in a pure state those oils

[1] *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 426.
[2] Koettstorfer, who originated this test as a means for detecting the adultera-
ion of butter, expressed his results in milligrammes of potash per gramme of fat,
.e. in parts per 1000, and, with the exception of Allen (*Comml. Org. Anal.*), most
authors have followed his example. The acetyl values of oils are similarly
expressed, but the Hehner and iodine values have always been expressed in
percentages. For the sake of uniformity, the percentage system is adopted for all
values given in this volume.

and waxes which have characteristic values, and, to a limited extent, to detect the adulteration of one fatty oil with another having a different saponification value.

II. Determination of the Saponification Value.

For the determination of this value the following reagents are required :—

Approximately seminormal alcoholic potash, made by dissolving about 18 grms. of the purest obtainable potash in 500 c.c. of pure rectified alcohol. As potash 'pure by alcohol' usually contains about 20 per cent. of water, this solution will be about seminormal in strength ; if anhydrous potash be used, 14 grms. would be enough.

If made with impure spirit, the solution will rapidly assume a red or brown colour and will then be unfit for use, but if made with pure rectified alcohol it will slowly acquire a pale yellow tint which in no way interferes with the test. No difficulty will be experienced in dissolving the potash in the strong alcohol if the following plan be adopted :—Introduce the potash and the alcohol into a 500 c.c. test mixer, insert the stopper, and invert the cylinder so as to bring the potash to the upper end. Then lay the cylinder upon the bench and raise the upper end upon a block at such an angle that the potash will not slide to the bottom ; it will then very rapidly dissolve. When solution is complete, well mix the contents of the cylinder, allow to stand over night, and filter through a dry filter paper into the reagent bottle, which should be closed by a rubber stopper and kept in a cool, dark cupboard.

Seminormal hydrochloric acid, accurately standardized with pure sodium carbonate, which has been heated to just below redness for five minutes and cooled in a covered platinum crucible in a desiccator immediately before weighing. 1 c.c. of strictly seminormal acid neutralizes 0·02807 grm. KOH.

Phenolphthalein solution. (See p. 216.)

(*a*) **In determining the saponification value of a fixed oil or fat,** 2·5 grms. are weighed into a small wide-necked flask and 25 c.c. of the seminormal potash solution are added from a pipette. Exactly the same volume of potash solution is then delivered into an empty flask of the same size and shape. The two flasks are closed by corks having a groove filed in the side for the escape of vapour. The 'blank' quantity is placed at once inside the water-oven. The flask containing the oil is first of all heated on a steam-bath until the alcohol commences to boil ; it is then agitated with a rotary motion, to and fro, so as to break up the oil into small globules and facilitate the saponification, care being taken not to splash the liquid up on to the cork. When (in the case of a pure fatty oil) the globules of oil have entirely disappeared, or when (in the case of a mixed fatty and mineral oil) the oil and alkaline solution have been thoroughly boiled and agitated together, the flask is placed inside the water-oven. After fifteen minutes have elapsed, the 'blank' quantity is taken out, mixed with about 1 c.c. of phenolphthalein solution, and carefully titrated with the seminormal acid until the crimson colour is just bleached ; the flask containing the saponified oil is then similarly treated, and from the relative volumes of acid used the saponification value is calculated as shown by the following example :—

TABLE LVIII.—SAPONIFICATION VALUES OF SOME OILS, FATS, AND WAXES.

Class.	Name of Oil, etc.	Saponification Value. KOH required to saponify 100 parts of the substance.
Vegetable Non-drying Oils and Fats.	Olive oil, .	18·5 –19·6 ; usually about 19·0 ˣ
	Olive kernel oil,	18·23–18·38
	Hazel nut oil, .	18·7 –19·7
	Ben oil, .	18·5 –18·8
	Arachis (earthnut) oil,	18·ᵗ –19·7
	Castor oil,	17·6 –18·7
	Japan wax,	21·4 –23·7
	Coconut oil,	24·6 –26·8
	Palm nut oil,	24·2 –25·5
	Palm oil, .	19·5 –20·6
	Cottonseed stearin,	19·5
Vegetable Semi-drying Oils.	Rape oil, .	17·0 –17·5
	Ravison oil,	17·8 –18·1
	Mustard oil (white),	17·0 –17·4
	Mustard oil (black),	17·3 –17·5
	Curcas oil,	19·2 –19·3
	Cottonseed oil, .	19·1 –19·7
	Sesamé oil,	18·8 –19·5
	Brazil nut oil, .	19·3
	Beech nut oil, .	19·1 –19·6
	Maize oil,	18·8 –19·3
	Cameline oil,	18·8
Vegetable Drying Oils	Linseed oil,	18·8 –19·5
	Hempseed oil, .	19·0 –19·3
	Poppyseed oil,	18·9 –19·8
	Walnut oil,	18·9 –19·7
	Nigerseed oil, .	18·9 –19·2
	Sunflower oil, .	18·8 –19·4
Animal Oils and Fats.	Neatsfoot oil, .	19·4 –19·9
	Lard oil, .	19·1 –19·6
	Tallow (beef, mutton, and home refined),	19·0 –19·8
	Bone fat, .	19·1 –19·5
	Lard,	19·5 –19·7
	Horse fat,	19·5 –19·7
Marine Animal Oils and Fluid Waxes.	Sperm oils (Southern and Arctic), .	12·3 –14·7
	Porpoise jaw oil, strained from solid fat, .	25·3 –27·2
	Porpoise jaw oil, unstrained,	14·4
	Dolphin jaw oil, strained from solid fat,	29·0
	Porpoise body oil,	19·5 –21·9
	Dolphin body oil,	10·7 –20·3
	Whale oil,	18·8 –19·4
	Seal oil, .	17·8 –19·6
	Cod-liver oil,	16·8 –19·3
	Other fish liver oils,	14·6 –19·1 †
	Menhaden oil, .	18·9 –19·3
	Sardine (including Japan fish) oil, .	18·9 –19·4
Waxes (solid).	Wool fat,	9·8 –10·2
	Spermaceti,	12·3 –13·6 g
	Beeswax,	8·8 –10·7
	Carnauba wax, .	7·8 – 8·4
Blown Oils.	Blown rape oil, .	19·5 – 20·8
	Blown ravison oil,	20·0
	Blown cottonseed oil,	21·8 –21·6
	Blown seal oil, .	22·1
Hydrocarbons.	Mineral oil,	nil.
	Vaseline, .	
	Paraffin wax and cerasin,	

* De Negri and Fabris, 203 samples.
† Liverseege (Analyst, 1904, p. 210) records a sample of 'shark oil' absorbing only

Weight of oil taken ; 2·5 grms.

Volume of $\frac{N}{2}$ acid used for the 'blank,' . . . 26·05 c.c.

„ „ „ sample, . . . 10·55 c.c.

Difference ; $=\frac{N}{2}$ KOH required for saponification, . 15·50 c.c.

Therefore, 100 grms. of oil required $15·5 \times 0·02807 \times 40 = 17·40$ grms. KOH for complete saponification; *i.e.* the saponification value is 17·40 per cent.

The quantity of potash used in this test should be largely in excess of the quantity required for saponification, and if it should be found on titrating with acid that the potash added has been nearly all used up, the test must be repeated, either with less of the oil or with a stronger potash solution. In general, correct results will be obtained by adhering to the proportions given above.

(*b*) *In testing mixed fatty and mineral oils*, especially when the proportion of mineral oil is large, it is safer to attach the flask, by means of a good ordinary cork, to a reflux condenser, and boil for an hour or more to ensure complete saponification, the 'blank' quantity of potash solution being boiled in the same way and for the same length of time. In testing two or more oils at the same time, if there are not enough condensers, the potash solution should be measured into all the flasks, and those which have to wait kept closed with rubber stoppers until condensers are available, each liquid being titrated with acid as soon as it has been removed from the condenser. Wool fat would not be completely saponified in this way, and must be heated in a closed bottle under pressure with double normal alcoholic potash for about two hours (see p. 227).

(*c*) The terms '*saponification value,*' '*Koettstorfer value,*' '*alkali value,*' employed by various authors, have the same meaning. The term '*saponification equivalent,*' used by Allen,[1] means the weight of oil or fat saponified by 56·1 parts of potash, or by one equivalent of any other alkali. Thus, the

saponification value (%) : 100 :: 56·1 : the saponification equivalent,

∴ the saponification equivalent $= \dfrac{5610}{\text{the saponification value}}$.

The saponification equivalent of any glyceride is one-third of the molecular weight; in the case of the ester of a monohydric alcohol it is identical with the molecular weight, and the same is true of the free fatty acids.

D.—APPROXIMATE ANALYSIS OF MIXED LUBRICATING OILS.

It is obvious that the composition of a mixture of mineral oil and a single known fatty oil can be calculated from the saponification

[1] *Comml. Org. Anal.*, vol. ii. pt.]i. p. 53.

value of the mixture. Thus, if a mixture known to consist of rape oil and mineral oil have a saponification value, per cent., of 8·2, the percentage of rape oil in the mixture must be nearly $8·2 \times 100 \div 17·3 = 47·4$, and the percentage of mineral oil $100 - 47·4 = 52·6$.

When the nature, and therefore the saponification value, of the fatty constituent is unknown, the possible error of the method becomes greater, but Gripper[1] has shown, by the analysis of several mixed lubricating oils, that the results obtained are sufficiently correct for commercial purposes when rapidity is of supreme importance. He adopts 20·08 per cent. as the mean saponification value of the fatty constituent, and, considering the extent to which blown rape oil is used in the preparation of commercial lubricating oils, this figure would be likely to give good results in, perhaps, the majority of cases. Very nearly the same result would be obtained by taking the whole number 20. Then, the saponification value, per cent. of the mixture, $\times 5$ is the approximate percentage of saponifiable oil, and the percentage of mineral oil is obtained by subtracting this number from 100.

After determining the saponification value, Gripper again raises the alcoholic liquid to the boiling-point and pours it on to a filter paper which has been saturated with boiling water. The alcoholic solution of soap, etc., quickly runs through, leaving the greater part of the hydrocarbon oil on the filter. After washing once with boiling water, the specific gravity of this oil is determined by the alcohol method (p. 178).

E.—DETERMINATION OF TOTAL UNSAPONIFIABLE MATTER.

If the solution obtained by saponifying a mixed fatty and mineral oil with potash or soda be shaken with an immiscible solvent, such as ether or petroleum ether, or if the dried soap be extracted with petroleum ether or chloroform, all the unsaponifiable hydrocarbon oil is dissolved out, and may be obtained in a separate state by evaporation of the solvent, and the amount determined by weighing.

Commercial fixed oils and fats, quite free from added hydrocarbons, contain small quantities of unsaponifiable substances which, under similar circumstances, are extracted by the solvent; but in most cases the natural unsaponifiable matters (chiefly phytosterol, cholesterol, etc.) do not amount to more than from 1 to 1·5 per cent. The waxes, however, such as sperm oil, wool fat, beeswax, and carnauba wax, yield on saponification, instead of glycerol, monohydric alcohols which dissolve in the ether and may amount to from 35 to 55 per cent. of the wax saponified. Shark liver oil also frequently yields on saponification considerable quantities of solid alcohols.

In the analysis of lubricants, therefore, the determination of the unsaponifiable matter is not only a means of separating and determining

the proportion of hydrocarbon oil present, but it is also a means of identifying sperm oil and the waxes, ascertaining their purity, and determining their proportion in mixtures.

I. General method for the determination of unsaponifiable matter in an easily saponifiable oil, fat, or fluid wax, such as rape oil, sperm oil, etc.

The following reagents are required :—

Caustic Soda Solution.—250 grms. of pure caustic soda from sodium are dissolved in cold water in a deep porcelain basin, and the solution, when cold, is made up to 500 c.c. if not clear, it may be filtered through ordinary filter paper. The solution is preserved for use in a bottle closed by a rubber stopper. 2 c.c. contain, approximately, 1 grm. NaOH.

Alcohol.—Methylated alcohol free from naphtha may be used, but pure rectified alcohol of 0·830 sp. gr. is preferable.

Ether.—Redistilled methylated ether of sp. gr. 0·725.

(*a*) **The Process.**—Pour about 10 c.c. of the oil into a very small lipped beaker and take the exact weight. Then take a deep porcelain basin, 5½ inches in diameter, and a glass rod, both dry, and pour oil out of the beaker into the basin until exactly 5 grms. have been transferred. If a little too much is poured, it can be returned to the beaker in drops on the end of the rod. A solid fat is weighed similarly, but is taken out of the beaker on a spatula, which is subsequently rinsed into the basin with a little boiling alcohol or a few drops of ether.

Mix, in a stoppered cylinder, 4 c.c. of the caustic soda solution and enough alcohol to make 50 c.c ; pour this into the basin, and boil *gently* over a small Argand-Bunsen flame, with stirring, until most of the globules of oil have disappeared. Then cover the basin with a clock glass and keep the liquid gently boiling until it has become concentrated to about 12–15 c.c., which should be made to take at least half an hour so as to ensure thorough saponification. If the liquid should concentrate too rapidly, add 25 or 50 c.c. more alcohol and boil down again. The basin should be supported on a perforated disc of asbestos millboard to protect the sides from being overheated by the flame. Pour the hot soap solution into a globular separating funnel of about 300 c.c. capacity (fig. 71),[1] previously heated by rinsing with hot water in order to prevent chilling and solidification of the soap solution, and rinse the basin with small quantities of very hot water until all the soap is transferred. The volume of liquid in the separator should not exceed about 70–90 c.c. Pour, carefully, on the still hot liquid about 100–120 c.c. of ether, insert the stopper, and whilst holding the stopper and tap firmly fixed, shake the separator, at first cautiously, under a running tap of cold water, for at least one minute, not too vigorously, so as to thoroughly mingle the ether and soap solution without emulsifying them. Then place the separator in a stand. One of four things will now happen.

Fig. 71.—Separating Funnel.

[1] Made by cutting all but about 1½ inches of the stem off a bulb funnel, and filing the end obliquely.

(α) The liquids will separate into two distinct layers, about equal in volume, the upper one an ethereal solution of the unsaponifiable matter and the lower a solution of soap. This is as it should be.

(β) The liquid will separate into *three* well-defined layers, or into two layers of which the upper is of much less volume than the lower. This shows that too much alcohol is present. Add small measured quantities of cold water, 5 c.c. at a time, and re-shake cautiously until the liquid separates into two layers only, of about equal volume.

(γ) The liquids will not separate, but present the appearance of a *nearly transparent* homogeneous fluid. Probably too much alcohol is present; if so, the cautious addition of small quantities of water, as in (β), will cause separation to occur.

(δ) The liquids form an *opaque viscid emulsion*. In this case there is probably not enough alcohol, and the remedy is to add more alcohol, 2 or 3 c.c. at a time, and cautiously mix until separation into two layers occurs either at once or on standing for a few minutes.

When the liquids have properly separated (allow about ten minutes for complete separation to occur) draw off the layer of soap solution into another separator.[1] Shake this again with ether (using about 70 c.c. this time), run it off into a third separator, and shake a third time with ether. Then mix all three ethereal layers in one separator, wash twice, each time with 10 c.c. of a 1 per cent. caustic soda solution containing 10 per cent. of alcohol, then wash six times with pure water, using 10 c.c. each time. Thoroughly drain off the water, pour the ethereal solution (in two portions) into a light, wide-necked, 8-oz. flask, previously weighed, and distil off the greater part of the ether from a hot water-bath. Then place the flask on the top of the water-oven, and let it stand there until the ether and water have entirely evaporated. The evaporation of the water may be hastened by surrounding the flask with a beaker from which the bottom has been removed, and by frequently running the liquid round the sides of the flask. Then let the flask cool, and weigh it. Replace it in the oven for ten or twenty minutes, cool, and re-weigh. Repeat this until practically constant. By subtracting the tare of the empty flask, the weight of unsaponifiable matter in the 5 grms. of oil taken is obtained.

If the above directions are carried out, the whole operation, from weighing out the oil to the final weighing of the unsaponifiable matter, can be completed within three hours. Ordinary ether is preferable to petroleum ether for extracting the unsaponifiable matter; it boils at a lower and a constant temperature, evaporates more readily, and leaves no residue. Petroleum ether can be purchased which is completely volatile at 60° C.; but it must always be tested, and, if found impure, must be re-fractionated, rejecting all that boils above 60° C. When ordinary ether is used, it may be completely evaporated at such a low temperature that light mineral oil, which is sometimes used for adulterating rape and other oils, can be detected and determined without appreciable loss. Lewkowitsch has pointed out that ordinary ether usually extracts larger quantities of soap than petroleum ether; but, for ordinary purposes, the amount of soap extracted when the process is conducted as described above is negligible. In cases where special accuracy is required, traces of soap and saponifiable matter contained in

[1] Before removing the stopper, drop a little ether upon the outside of the separator and blow upon it, so as to cool the glass by evaporation; this will reduce the pressure of the ether vapour inside, and will prevent drops of liquid from being expelled when the stopper is removed.

the product of the first extraction may be removed by boiling it with alcoholic soda and re-extracting with ether; or, the unsaponified matter may be incinerated, as recommended by Lewkowitsch, and the soap present calculated from the alkalinity of the residue. Petroleum ether is not such a good solvent for some wax alcohols as ordinary ether. Thus, Lewkowitsch describes an experiment in which a sample of shark liver oil gave 10 per cent. of unsaponifiable matter, consisting of wax alcohols from spermaceti, when ordinary ether was employed, whereas petroleum ether only extracted from 1·38 to 3·73 per cent.

(b) *Modification in presence of much Mineral Oil.*—When much mineral oil is present, saponification in a basin is not a satisfactory method, because the oil does not entirely dissolve, but visible drops of mineral oil remain suspended in the liquid, and a more vigorous and longer boiling is necessary in order to ensure complete saponification. In such cases, it is better to weigh the oil into a flask and boil it with the alcoholic soda solution under a reflux condenser for an hour or more. Then pour the contents of the flask into a basin, boil down gently to 10–15 c.c., and proceed exactly as directed above, rinsing the flask as well as the basin into the separator, first with a little hot water and then with ether from the wash bottle.

(c) *Modification in presence of Wool Fat.*—Wool fat and lubricants containing it must be heated with alcoholic soda solution of double normal strength in a closed bottle under pressure for about two hours to insure complete saponification.[1] An ordinary 4-oz. reagent bottle of fairly thick glass answers very well for this purpose, and after the oil or fat and the alkaline solution have been introduced[2] an indiarubber stopper[3] is inserted and tied firmly down with string, leaving a loop at the top. This loop is suspended from a glass rod or stout brass wire fixed horizontally over a can of warm water, so that the bottle is immersed up to the neck in the water, which is then raised to the boiling-point and kept gently boiling. If the bottle will not sink sufficiently, a strip of lead may be wrapped round it and fastened by an indiarubber band. The bottle is removed from the water occasionally and the contents well mixed by circular agitation, taking care not to splash any liquid on to the rubber stopper. When saponification is complete the bottle is allowed to cool, the stopper is then taken out, the liquid is poured into a basin and proceeded with as directed above.

The formation of a *layer of white insoluble flocks* between the aqueous and ethereal liquids is characteristic of wool fat, and often indicates its presence. Lewkowitsch has shown that these flocks consist of an insoluble soap formed from fatty acids of high molecular weight; they do not belong, therefore, to the unsaponifiable matter, and should be separated from the washed ethereal liquid by filtration through a small dry filter paper. The same device is often useful for removing drops of water which might otherwise find their way into the distilling flask

(d) *Modification in presence of Beeswax.*—Owing to the sparing solubility of myricyl alcohol in most cold solvents, the above method cannot be applied to the analysis of beeswax, carnauba wax, and substances containing large quantities of myricyl alcohol.[1] When beeswax and carnauba wax are boiled

[1] Lewkowitsch, *Jour. Soc. Chem. Ind.*, xi. (1892), p. 137; Herbig, *ibid.*, xiii. (1894), p. 1068.
[2] For 5 grms. of fat use 4 c.c. of 50 per cent. caustic soda solution diluted to 25 c.c. with absolute alcohol.
[3] This must be pure rubber, free from substitutes.
[4] Allen, *Comml. Org. Anal.*, vol. ii. pt. i. p. 49.

with alcoholic soda solution under a reflux condenser, saponification readily takes place, and a clear or almost clear solution is obtained in a short time, but, immediately the liquid begins to cool, not only the wax-alcohol but the soap (sodium cerotate) solidifies on the sides of the flask, and before the contents have become nearly cold they form an almost solid mass. The best way to proceed in such cases (which are unlikely to occur in connection with the analysis of lubricants) is to extract the *dry* soap with chloroform as recommended by Horn and Grittner.[1] Five grms. of the sample are boiled, until thoroughly saponified, with 4 c.c. of 50 per cent. caustic soda solution and 100 c c of alcohol in a flask connected to a reflux condenser. The boiling-hot solution is poured into a basin, the flask well rinsed out with small quantities of boiling-hot alcohol, and the liquid evaporated to a small bulk over a steam-bath, with stirring. Some coarsely powdered pumice stone[2] is then added, and the contents of the basin are evaporated to dryness with continual stirring, so as to reduce the residue to small grains, and well dried in the steam oven. Any soap adhering to the basin is scraped off with a spatula, and the entire residue is transferred to a Soxhlet apparatus and extracted with chloroform, which is subsequently evaporated and the residue weighed. The basin is rinsed into the apparatus with hot chloroform before the extraction is commenced. Two hours' extraction, if the apparatus is working well, will dissolve all the alcohols from 5 grms. of saponified beeswax ; only traces are extracted in the second hour.

Sufficient pumice must be added to enable a granular non-pasty residue to be obtained. Sand, which is sometimes recommended, is less suitable than coarse pumice, and must, according to Grittner, be purified from calcium carbonate by washing with hydrochloric acid, in order to prevent the formation of lime soaps which are soluble in chloroform. Chloroform is used in preference to petroleum ether, as it does not dissolve the soda soap. It is, however, desirable to make sure that the unsaponifiable matter is free from soap by determining the ash of a portion, as recommended by Lewkowitsch. It is also desirable before evaporating the soap solution to add sufficient sodium bicarbonate to convert the excess of caustic soda into carbonate (2·1 grms. NaHCO₃ for 1 grm. NaOH). If petroleum ether be used, this is essential.

II. Determination of Small Quantities of Saponifiable Matter in Mineral Oils.

In the analysis of mineral oils containing small quantities of fat or resin, it is preferable to determine the fatty or resin acids as described in section G (p. 235), and the hydrocarbon oil by difference. The percentage of fatty acids obtained, divided by 0·95, will give, approximately, the percentage of fatty oil.

F.—COMPOSITION AND IDENTIFICATION OF UNSAPONIFIABLE MATTERS.

The unsaponifiable matter obtained in the analysis of lubricants may be expected to contain—

[1] *Jour. Soc. Chem. Ind.*, vii. (1888), p. 696, and ix. (1890), p. 772.
[2] The fragments of pumice should pass through a sieve having 11 meshes to the linear inch, and should contain no powder which will pass a 24-mesh sieve.

Hydrocarbons; including

> **Mineral oil** from petroleum or shale,
> **Rosin oil,**
> (**Neutral tar oil** from coal tar),
> **Hydrocarbons** from distilled wool grease,

} Liquid at the ordinary temperature.

> **Paraffin wax or cerasin,**
> **Vaseline,**

Wax Alcohols, from sperm oil, wool fat, etc.,
Cholesterol, from wool fat, liver oils, and all other animal oils and fats,
Isocholesterol from wool fat,
Phytosterol, from vegetable oils and fats,
Colouring matter (*traces*),
Unsaponified oil or fat,
Soap.

} Solid or semi-solid at the ordinary temperature.

1. **Hydrocarbons,** whether liquid or solid, may be identified by their sparing solubility in alcohol. If a small drop of the unsaponifiable matter on the end of a thin glass or platinum rod, or in a platinum wire loop, be immersed in a little cold rectified alcohol in a test-tube which is held up between the eye and a window, pure hydrocarbon oil will show no sign of solution, and the drop will probably appear fluorescent at the edges; but, if wax alcohols from sperm oil be present they will quickly dissolve and cause visible stream lines in the liquid. If the unsaponifiable matter be solid the solvent alcohol may be gently warmed, sufficiently to melt it.

(*a*) *Fluorescence* is a very characteristic property of hydrocarbon oils, though all do not show it. Distinct fluorescence of the unsaponifiable matter or of its ethereal solution proves the presence of hydrocarbons; but a non-fluorescent appearance does not prove their absence. If the fluorescence be not readily observed, Allen recommends laying a glass rod, previously dipped in the oil, on a table in front of a window, so that the oily end of the rod projects over the edge of the table away from the window and can be seen against the dark background of the floor. Another plan is to make a broad streak of the oil on a piece of black marble, or on a sheet of glass lying on black paper or cloth. The fluorescence of hydrocarbon oil is, as a rule, greatly intensified by solution in ether, which frequently leads to its detection while the unsaponifiable matter is being extracted. Mineral oils which have been 'debloomed' by chemical treatment (see p. 98) regain their fluorescence by treatment with an equal measure of strong sulphuric acid (*Allen*).

(*b*) Hydrocarbon oils are unacted upon when submitted to the *acetylation test* (p. 243). If the unsaponifiable matter after treatment with acetic anhydride has no saponification value, hydrocarbons alone are present.

(*c*) If the unsaponifiable matter consists entirely of hydrocarbons, the *specific gravity* should be determined by the alcohol method

(p. 178). Mineral lubricating oils (including also vaseline and paraffin wax) usually range in specific gravity from about 0·860 to about 0·947 at 60° F., though the sp. gr. may go as high as 0·99; rosin oil is heavier, usually ranging from about 0·96 to 1·01 ; tar oils always exceed 1·0 in specific gravity and will therefore sink in water. For the examination of mixtures see section S (p. 295).

(*d*) **Vaseline** at the ordinary temperature is semi-solid, soft, and amorphous ; **paraffin wax** is more or less hard and crystalline. Allen has shown that although in the solid state these substances are nearly of the same specific gravity, their densities in the liquid state at the temperature of boiling water are widely different ; his results are summarized in the following table :—

Description.	Specific Gravity.	
	Solid, at $\frac{15 \cdot 5'}{15 \cdot 5'}$ C.	Melted, at $\frac{99'}{15 \cdot 5}$ C.
Vaseline (9 samples), . . .	0·856–0·909	0·804–0·855
Paraffin wax (7 samples), . .	0·867–0·911	0·748–0·757

Allen's results at 99° were obtained with the Westphal balance, and as no correction was made for the expansion of the plummet, they are about 0·002 too high (*Alder Wright*).

(*e*) Mineral oils absorb variable amounts of *iodine*, according to the proportion of unsaturated hydrocarbons contained in them. Paraffin wax and cerasin absorb less than 5 per cent. of iodine, vaseline absorbs rather more, and the fluid oils absorb up to 23 per cent. (see Table LXVIII., p. 256). Rosin oils absorb from 43 to 48 per cent. (*Valenta*).

II. The **Wax Alcohols** which most frequently occur in lubricants are those derived from *sperm* or *bottlenose oil*. Their nature is at present unknown. When obtained from pure sperm or bottlenose oil, they are crystalline and almost colourless, having only a very pale greenish yellow tint. Their consistence at the ordinary temperature is that of solid, soft fat, and they melt at 23·5° to 27·5°C. They dissolve easily in warm rectified alcohol, and the solution remains clear on cooling ; if, therefore, the 'unsaponifiable matter' from 5 grms. of oil is completely soluble in about 2 c.c. of cold rectified alcohol of sp. gr. 0 834, and remains clear on adding 50 c.c. more rectified alcohol,[1] it cannot contain an appreciable quantity of hydrocarbons, and probably consists entirely of the mixed alcohols from

[1] Nash (*Analyst*, 1904, p. 3) has shown that a solution of sperm oil alcohols in absolute alcohol, and even in rectified alcohol, unless much diluted, dissolves mineral oil freely. Absolute alcohol must, therefore, not be used for detecting mineral oil in sperm oil.

sperm or bottlenose oil.   These alcohols may be further identified by their iodine value, 60–70 per cent. ; by their specific gravity at $\frac{100°}{100°}$ C., about 0·827 ; and by the acetylation test described on p. 243. When mixed with twice their volume of acetic anhydride, they dissolve easily when gently warmed, and the solution remains clear on cooling ; the mixed acetates have a saponification value of 16·1 to 19·0 per cent. according to Lewkowitsch.

III. **The Mixed Alcohols from Wool Fat** are pale yellow, have the characteristic odour of wool fat and the consistence of wax. Melting-point, 44°–48° C. Iodine value, about 35–40 per cent. Specific gravity at $\frac{100°}{100°}$ C., about 0·957. They dissolve readily in warm rectified alcohol ; but on cooling even a dilute solution, partial precipitation occurs.   By fractional crystallization from a hot, strong solution in alcohol or ether-alcohol, crystals of cholesterol are obtained, which may be identified by their melting-point, crystalline form, and colour reactions (see p. 292).   The mixed acetates formed by boiling the alcohols with acetic anhydride require from 15·1 to 16·1 per cent. of potash for saponification.   These properties easily distinguish the wool fat alcohols (when pure) from those of sperm and bottlenose oils.

IV. **Beeswax and Carnauba Wax** are unlikely to occur in the analysis of lubricants.   The presence of either wax could scarcely fail to be indicated by the insoluble character and comparatively high melting-point of the myricyl alcohol formed by saponification.   This alcohol, mixed in the case of beeswax with some hydrocarbons, is the chief constituent of the 'unsaponifiable matter' of both waxes ; it is white or pale yellow in colour, very hard and brittle, soluble with difficulty in even boiling alcohol, and almost entirely crystallizes out on cooling.   Melting-point of the products from beeswax, 76° (owing to the hydrocarbons present), and from carnauba wax, 85°.   Saponification value of the mixed acetates from beeswax, 10 per cent., and from carnauba wax, 12 per cent.

V. **Cholesterol and isocholesterol** form a large proportion of the unsaponifiable matter of wool fat.   Cholesterol also occurs in smaller quantity in various oils (shark liver oil, cod-liver oil, etc.), and is characteristic of animal oils generally.   On the other hand, a very similar substance, **phytosterol**, the 'cholesterol of plants,' is found in the unsaponifiable matter of rape and other vegetable seed oils, and olive oil.   All three substances are monatomic alcohols of the aromatic series, generally regarded as isomeric, and having the formula $C_{26}H_{44}O$ They are colourless and tasteless crystalline bodies, of high melting-point, insoluble in water, sparingly soluble in cold alcohol, but easily soluble in hot alcohol, ether, and chloroform. They may be distinguished, when in a pure state, by their melting-points and crystalline forms, which are given in the following table :—

TABLE LIX.

	Cholesterol.	Isocholesterol.	Phytosterol.
Melting-point, °C.	148·4–150·8 (*Bömer.*) *	137–138	138–143·8 (*Bömer.*) *
Crystalline form,	Thin rhombic plates of $C_{26}H_{44}O$ + H_2O from hot alcohol and ether. ——— Anhydrous needles from chloroform.	Flocks from dilute alcohol ; a jelly from concentrated alcoholic solution ; needles from ether.	Tufts of needles $C_{26}H_{44}O$ + H_2O from hot alcohol ; anhydrous needles from ether and chloroform.

* Point of complete fusion (corrected).

According to Bömer, cholesterol and phytosterol when present together cannot be separated by crystallization. The melting-point of the mixture in general approximates to that calculated from the melting-points of its components. The mixture crystallizes in one form only, the crystals either approximating in form to phytosterol crystals or, if cholesterol be present in the greater proportion, differing in form from the crystals of either body.

To obtain the crystals, the unsaponifiable matter from 50 grms. of oil should be boiled with a small quantity of alcohol and the solution filtered hot. The crystals deposited on cooling must then be purified by repeated re-crystallization, and examined under the microscope. They should be compared with the crystals obtained in the same way from pure samples of, say, rape oil (*phytosterol*), cod-liver oil (*cholesterol*), and wool fat (*cholesterol* and *isocholesterol*). (Compare Salkowski, *Jour. Chem. Soc.*, 1888, Abs. 201.)

For the detection of vegetable oils in animal oils, Bömer [1] determines the melting-point of the cholesterol (phytosterol) acetate. The points of complete fusion of the pure esters are as follow :—

Cholesterol acetate, . . . 114·3° – 114·8° C. (corr.)
Phytosterol „ . . . 125·6° – 137° C. (corr.)

The Process.—The unsaponifiable matter is isolated from 100 grms. of the oil or fat by saponification and shaking out the soap solution with ether, and is purified by resaponification and again extracting with ether. The extracted matter is then dissolved in a minimum quantity of absolute alcohol, allowed to crystallize, and the crystals are examined microscopically to determine whether they consist of phytosterol, cholesterol, or a mixture ; they are then returned to the alcohol and the latter is evaporated off. 2–3 c.c. of

[1] *Zeits. Untersuch. Nahr. Genussm.*, 1901, iv. 1070.

acetic anhydride are next poured over the dry residue, the dish is covered, the liquid is heated over a small flame until it boils, and the excess of acetic anhydride is evaporated off over a water-bath.   The acetic esters thus obtained are dissolved in hot absolute alcohol (10 to 25 c.c. for 0·1 to 0·3 grm. of esters), a few c.c. more alcohol being added to prevent immediate crystallization, and the clear solution is left to slowly evaporate at the ordinary temperature.   When above half of it has evaporated, the crystals are collected on a very small filter and recrystallized from 5 to 10 c.c. of absolute alcohol, the process of recrystallization being continued so long as the material lasts.   The melting-point of the crystals is determined after the third and each subsequent crystallization, and if the temperature of

TABLE LX.—PERCENTAGE OF UNSAPONIFIABLE MATTER OBTAINED FROM SOME FIXED OILS, FATS, AND WAXES.

Name of Oil, etc.	Unsaponifiable Matter per cent.	
Olive oil,	0·75–1·50	
Arachis oil,	0·54–0·91	
Castor oil,	0·30–0·37	
Palm oil,	1·25	
Rape oil,	0·58–1·30	
Ravison oil,	1·45–1·66	
Cottonseed oil,	0·73–1·85	
Sesamé oil,	0·95–1·32	
Maize oil,	1·35–1·71	Under
Linseed oil,	0·60–1·28	2 per cent.
Hempseed oil,	1·00	
Poppyseed oil,	1·15	
Tallow,	0·50	
Lard,	0·23–0·30	
Porpoise oil,	0·67	
Seal oil,	0·24–1·4	
Sardine oil,	0·56–1·44	
Whale oil,	0·65–3·7	
Cod-liver oil,	0·46–2·68	
Shark liver oil,	Very variable ; from 0·7% to 21·8% have been recorded.*	
Menhaden oil,	0·60– 2·2	2 per cent. and over.
Sperm oil,	36·3–41·5	
Arctic sperm oil,		
Wool fat,	33·7–55·1	
Spermaceti,	51·5	
Beeswax,	52·3–55·3	
Carnauba wax,	52·4–55	

* See also note at foot of page 222.

complete fusion be 117° C. (corr.) or higher, Bömer regards the presence of vegetable oil as certain. He states that from 1 to 2 per cent. of vegetable oils containing considerable quantities of phytosterol, such as cottonseed, arachis, sesamé, rape, hemp, poppy and linseed oils, can be detected in animal oils by means of this test ; and of other vegetable oils, such as olive, palm, and palm kernel, from 3 to 5 per cent. can be detected.

For the separation of cholesterol and phytosterol from mixtures of mineral oils and fixed oils, Marcusson saponifies, and shakes the alcoholic solution first with petroleum spirit to extract the mineral oil. He then drives off the alcohol and shakes with ethyl ether to extract the cholesterol and phytosterol.

The test is based upon Bömer's observation that the higher aliphatic alcohols are not completely extracted from an alcoholic soap solution by petroleum ether.

Gill and Tufts (*Jour. Amer. Chem. Soc.*, xxv. 551) state that maize oil contains another alcohol, **sitosterol**, by which it can sometimes be identified as an adulterant in cottonseed oil.

Cholesterol gives several characteristic colour reactions (see p. 292) which distinguish it from isocholesterol, but not from phytosterol, which gives the same reactions.

TABLE LXI.—PROPERTIES OF THE MIXED ALCOHOLS, ETC. ('UNSAPONI-FIABLE MATTER') OBTAINED FROM WAXES.

Name of Wax, etc.	Properties of Mixed Alcohols, etc.				Saponifica-tion Value of the Mixed Acetates, per cent.
	Melting-point, °C.	Specific Gravity at 100° C. / 100°	Iodine Value.	Increase of Weight on Acetylating, per cent.	
Sperm oil, ⎫ Arctic sperm oil, ⎭	23·5°–27·5°	0·827	59·5–69·3	15·7	16·1–19·0
Wool fat, . .	44°–48°	0·957	35–40	12·2–12·7	15·0–16·1
Beeswax, .	75°–76°	0·8239	..	6·5– 7·7	9·9–10·3
Carnauba wax, .	85°	0·4826		10·2	12·3
Cholesterols (theory), ...			68·3	11·3	13·55
,, (experimental results by Lewkowitsch),			67·7	..	13·5

Note.—Some of the results in this table were obtained with single samples of the waxes in question, and therefore require confirmation.

VI. **Unsaponified oil or fat** will not occur in more than traces if saponification has been properly carried out, and **Soap** should not occur at all. If there be any reason to suspect the presence of either, the ether residue must be purified by boiling it with alcoholic soda (say 2 c.c. of 50 per cent. NaOH solution and 25 c.c. alcohol)

under a reflux condenser for half an hour and re-extracting with ether after evaporating off the alcohol and diluting with water. If wool fat be suspected, the resaponification must be conducted under pressure with alcoholic soda of double normal strength.

G.—DETERMINATION AND IDENTIFICATION OF THE SAPONIFIABLE OIL IN MIXED OILS.

In the analysis of lubricating oils consisting of a mixture of mineral oil and fixed oil, it is usually sufficient to determine the saponifiable oil by difference. But it is often necessary to liberate the fatty acids from the soap solution, in order to identify the fixed oil, and this may easily be done quantitatively, giving a number from which the percentage of fixed oil can be calculated. The details of manipulation are a continuation of the process for determining the total unsaponifiable matter. (F, p. 224.)

The soap solution, which has been freed from mineral oil and other unsaponifiable matter by shaking three successive times with ether, is mixed with the first two aqueous washings of the mixed ethereal liquids and treated with a sufficient excess of dilute sulphuric acid to decompose the soap and liberate the fatty acids. The acid liquid is mixed with 50–70 c.c. of ether, well shaken in the separator, and, after allowing sufficient time for the ether to rise, the aqueous portion is drawn off into another separator, where it is again shaken with ether. The ethereal liquids are mixed together in one separator, thoroughly washed by shaking six times with 10 c.c. of pure water each time, then poured into a tared flask, and the bulk of the ether distilled off. The flask is then placed on the top of the water-oven and heated, until all water and ether have evaporated and the weight remains practically constant.

In the absence from the original sample of the following—

> *Sperm and bottlenose oils,*
> *Porpoise and dolphin jaw oils,*
> *Shark liver oil,*
> *Palm nut and coconut oils,*
> *Wool fat,*
> *Blown oils,*
> *Soap,*
> *Resin,*
> *Free fatty acids,*

the percentage of fatty acids obtained, ÷ 0·957, will give, approximately, the percentage of fatty oil in the sample. Fatty acids existing in the original sample, either in the free state or as soap, must previously be separated as described in the analysis of greases (p. 328). Rosin acids, if present, must be determined by Twitchell's process (p. 238) and the amount deducted.

If the saponifiable oil consist entirely of blown rape or cottonseed oil the divisor becomes approximately 0·85 instead of 0·957, but special washing with hot water is required to remove the soluble fatty acids (see p. 237). In the presence of sperm oil and wool fat the problem becomes more complicated. The unsaponifiable matter in that case contains wax alcohols, and must be analysed by the acetylation process (p. 245).

As there is no known means of separating, without decomposition, a fixed oil or fat from a heavy mineral oil, the identification of the fixed oil in such mixtures depends upon the identification of the mixed fatty acids. For this purpose, the following determinations are available :—

1. *The melting-point* (table on p. 205).

2. *The sp. gr. at* $\dfrac{100^{\circ}}{100^{\circ}}$ *C.* (table on p. 185).

3. *The iodine value* (table on p. 255).

4. *The saponification or neutralization value.*

The fatty acids used for the determination of the iodine value must not have become oxidized, otherwise a low result will be obtained. After distilling off the ether the flask should, therefore, be closed by means of a cork carrying two tubes, in order that a current of dry carbon dioxide gas may be passed through the flask while heating on the steam-bath.

The saponification or neutralization value is best determined in the same manner as the saponification value of an oil or fat (p. 221), viz.—by heating 2·5 grms. with approximately seminormal alcoholic potash in excess, and titrating back with accurate seminormal hydrochloric acid. Theoretically, it should be sufficient to dissolve the fatty acids in alcohol and neutralize with standard potash solution in the cold, but if any undecomposed esters, or lactones, are present, a low result is obtained unless the potash be in excess and the liquid heated.

In the absence of soluble fatty acids, the neutralization value of the mixed fatty acids multiplied by the Hehner value of the oil will give the saponification value of the oil, *i.e.* the neutralization value × 0·957 will give, approximately, the saponification value of the oil or fat from which the fatty acids have been derived.

H.—INSOLUBLE FATTY ACIDS (HEHNER VALUE).

The process for determining the *total fatty acids* described in the preceding section (p. 235) is based upon the assumption that they are entirely, or almost entirely, insoluble in water and non-volatile, and such is, as a rule, the case. A few oils and fats, however, contain a considerable proportion of soluble and volatile fatty acids, notably cow's butter, dolphin jaw oil, and porpoise jaw oil. In such cases, the insoluble acids must be determined by a special process. Hehner was the first to show that the percentage of insoluble fatty acids contained

in genuine butter fat is fairly constant, and that by its determination the adulteration of butter with foreign fats can be detected; the percentage of insoluble fatty acids contained in an oil or fat is therefore known as the '*Hehner value.*'

It has been shown [1] that the changes caused by 'blowing' oils include a partial conversion of the insoluble acids into soluble and volatile acids; the presence, therefore, of 'blown' oil in castor oil would be indicated by a reduction of the percentage of insoluble fatty acids, of which genuine castor oil contains upwards of 95 per cent.

To determine the Hehner value of a fixed oil or fat, the fatty acids must be washed with boiling water until the washings are no longer acid. The following is a convenient method of operating :- Saponify 5 grms. of the oil with alcoholic soda, as directed in E, I. (p. 225), and after saponification is complete, evaporate to dryness over a steam-bath, and heat to remove alcohol. Dissolve the soap in hot water, and rinse the solution into a beaker-flask, the total volume being about 250 c.c. Liberate the fatty acids with dilute sulphuric acid, allow to stand on the steam-bath until the fatty acids have melted to a clear layer upon the surface of the liquid, then pour the whole carefully into a separating funnel previously rinsed with hot water. Support the separator over a wet filter paper contained in a jacketed hot-water funnel, and allow the clear liquid to run into the filter at a sufficient speed to keep it nearly full. The filtrate should be bright. Do not allow the oily layer to pass on to the filter, but return it to the original beaker-flask, and having added about 150-200 c.c. of boiling water, thoroughly churn the fatty acids and water together by circular agitation. Allow to stand again until the acids have risen, carefully decant into the separator, and run the aqueous portion through the wet filter as before. Repeat this washing five times more, but collect the last washing in a separate vessel, add a few drops of phenolphthalein solution, and find how much decinormal soda is required to produce a pink colour. Make a similar experiment with the same quantity of the hot distilled water used in washing the fatty acids. If practically the same number of drops are required in both experiments (disregard a difference of one or two drops) the washing is complete. When this is the case, allow the insoluble fatty acid layer to pass on to the filter paper, and let the water drain away ; well drain, also through the filter, the separator and the beaker-flask. So long as the paper remains thoroughly wet the fatty acids will not run through the paper. Transfer the wet filter paper containing the fatty acids to a dry funnel supported over a small weighed beaker, and place it in the water-oven until the filter has dried and the greater part of the fatty acids have drained through into the beaker. Then place the funnel containing the oily filter paper over a weighed flask, and when cold, thoroughly wash the paper with ether, allowing the latter to run into the flask, also rinse the separating funnel and the beaker-flask [2] with ether, passing the liquid through the same filter paper. Then distil off the ether, and heat both the flask and the small beaker until constant in weight. Deduct the weights of the two vessels, and the difference is the weight of the insoluble fatty acids.

In the presence of hydrocarbons or waxes, the soap solution obtained by saponification must first be extracted with ether, as described in E, I. (p. 225),

[1] See p. 122.
[2] These may be previously dried by placing them on the water-oven, or they can be rinsed with ether while wet.

then poured into a basin, gently heated over a steam-bath, with a cover on the basin, to expel the dissolved ether, thoroughly boiled to evaporate the alcohol, and then acidified and treated as described above.

Qualitative Preparation of Insoluble Fatty and Rosin Acids.—If it be required merely to prepare the insoluble fatty and rosin acids, without making a quantitative determination, the following method may be employed :— Saponify in a basin, by thorough boiling with alcoholic soda, a roughly weighed quantity of the oil, sufficient to give rather more than the required quantity of fatty acids, using for every 5 grms. of oil 2 grms. of caustic soda (4 c.c. of a 50 per cent. solution). Dissolve the soap in boiling water, and boil until alcohol is expelled. Add sufficient dilute sulphuric acid to liberate the fatty acids, gently boil until they form a clear layer on the surface of the liquid, then, by means of a large pipette with a flexible mouthpiece, draw off the watery fluid. Boil the fatty acids in the basin several times with water, drawing off the water with the pipette each time, then pour them on to a wet filter contained, if necessary (*i.e.* if the fatty acids have a high melting-point), in a hot-water funnel, and wash with boiling water until the washings are practically neutral to litmus or phenolphthalein. Pierce the filter, collect the acids in a dry beaker, and heat in the water-oven until quite clear and free from visible water.

Table LXII. contains the Hehner values of most oils and fats which are likely to occur in lubricants.

I.—DETERMINATION OF ROSIN (COLOPHONY).

The fatty acids obtained by either of the processes described in sections G and H include the rosin acids, if rosin be present. If a determination of the rosin be desired, Twitchell's process [1] is the best to adopt. It depends upon the fact that when a solution of fatty acids in absolute alcohol is saturated with hydrochloric acid gas the ethyl esters of fatty acids are formed. Rosin acids similarly treated in the cold are practically unacted upon, and can be separated from the esters by treatment with weak caustic soda solution in the cold, which dissolves the rosin acids, the esters remaining insoluble. The details of the process are as follow :—

From 2 to 3 grms. of the melted mixture of fatty and rosin acids are poured into a dry tared conical flask of about 8 ozs. capacity, and, when cold, the weight is accurately ascertained. The acids are dissolved in absolute ethyl alcohol,[2] using 10 c.c. for every gramme of acids, and dry hydrochloric acid gas, in a moderate stream, is passed through the solution until saturated, the flask being kept quite cold by immersion in a basin of cold water.[3] The hydrochloric acid gas may be prepared in a dry state by acting upon lumps of fused salt with concentrated sulphuric acid, and may then be passed direct into the liquid. The gas is rapidly absorbed, and the

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[1] *Jour. Soc. Chem. Ind.*, x. (1891), p. 804.

[2] Methyl alcohol is said to give lower results than ethyl alcohol.

[3] Evans and Black recommend the use of a tall cylinder surrounded by iced water. Temperature must not rise above 20° C., nor must the stream of hydrochloric acid be too rapid ; otherwise low results are obtained. *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 689 ; also *Analyst*, xx. (1895), p. 60.

TABLE LXII.—HEHNER VALUES.

Name of Oil or Fat.	Hehner Value. Percentage of Insoluble Fatty Acids.
Most vegetable and terrestrial animal oils and fats, except wool fat, . . .	95–97 Average about 95·7
Palm nut oil, ...	91·1
Coconut oil, ...	83·8–90·5
Marine animal oils, except sperm and shark liver, but including porpoise body and dolphin body oils, . . .	92·8–95·5 Average about 94·1
Porpoise jaw oil, ...	68·4 and 72·1
Dolphin jaw oil, ...	66·3
Blown rape oil, ...	84·7
„ cottonseed oil, ...	85·5 *
„ linseed oil, ...	86·7
„ seal oil, ...	73·4

* Fox and Baynes ; mean results.

esters separate in oily drops. When the alcoholic liquid is saturated (from 30–45 minutes are required), the flask is allowed to stand about half an hour longer to ensure complete esterification. It must not stand too long, otherwise low results are obtained. The liquid is then diluted with about five times its volume of boiling water, and heated on the steam-bath until some of the alcohol has evaporated and the esters, with the rosin acids in solution, form a clear layer upon the surface. The contents of the flask are poured into a separating funnel, and the flask as well as the gas delivery tube are rinsed with ether, which is poured into the separator. About 50 c.c. more ether are added, the contents of the separator are cooled, well shaken, and allowed to stand for the ether to rise. The acid liquid is drawn off into another separator and shaken again with a little ether, which is added to the first, and the ethereal solution is then washed once with about 10 c.c. of cold water, which is drawn off. It is then shaken in the funnel with 50 c.c. of dilute caustic soda solution containing 1·0 grm. of caustic soda and 10 c.c. of alcohol in 100 c.c., by which the rosin acids are immediately saponified and dissolved. After drawing off the alkaline liquid into a second separator, the ethereal solution is again shaken with about 20 c.c. more of the weak soda solution, which is added to the first, and the whole is then decomposed with dilute sulphuric acid and shaken with ether to dissolve the liberated rosin acids. The ethereal solution, after washing several times with small quantities of cold water, is run through a dry filter paper into a weighed flask, the ether is evaporated, and the residual rosin acids are heated in the water-oven until constant in weight. They should be quite hard and brittle. The weight obtained, multiplied by 100 and divided by the weight of mixed acids taken, gives the percentage of rosin acids.

Lewkowitsch,[1] who has extensively investigated this process, finds that the amount of rosin acids generally falls short of the truth.

[1] *Jour. Soc. Chem. Ind.*, xii. (1893), p. 503.

Evans and Black conclude that the loss is mainly due to unsaponifiable matter contained in rosin, which is not dissolved by the caustic soda solution. Six samples of rosin were found by them to contain from 5·0 per cent. to 9·71 per cent. of gummy matter unsaponifiable by alcoholic potash.

J.—VOLATILE FATTY ACIDS (REICHERT AND REICHERT-MEISSL VALUES).

The Reichert Process.—As has already been stated, a few oils and fats yield a considerable proportion of fatty acids soluble in water, and volatile when the liquid is distilled. By distillation in a current of steam, complete separation of the volatile and non-volatile acids can be effected,[1] but the process is very tedious. In Reichert's process only a portion of the volatile acids are distilled over, but by working under strictly defined conditions uniform results are obtained

In the process as originally described,[2] 2·5 grms. of the fat were saponified with an alcoholic solution of caustic soda, the alcohol was completely evaporated off, the soap dissolved in 50 c.c. of water, decomposed by adding 20 c.c. of dilute sulphuric acid and distilled until exactly 50 c.c. had come over. The distillate was then mixed with a few drops of litmus solution and titrated with decinormal alkali, the number of cubic centimetres required being recorded. Under these conditions, the distillate from cow's butter required not less than 13 c.c. of decinormal acid for neutralization, while the fats used in the manufacture of artificial butter required less than 0·5 c.c.

The Reichert-Meissl Process.—Reichert's process has undergone a variety of modifications in detail,[3] and as now carried out saponification is generally effected with a mixture of caustic soda solution and glycerol (*Leffmann* and *Beam*), by which the evaporation of alcohol is avoided ; also 5 grms. of fat are used instead of 2·5 grms. (*Meissl*), by which the volume of standard acid used in titrating is nearly, but not quite, doubled. This process, which is chiefly useful in the analysis of butter, is required in the analysis of such lubricants as porpoise oil ; it may also find occasional application in the detection of blown oils. The following reagents are required :—

1. *Glycerol-Soda.*—Made by mixing together 30 c.c. of aqueous caustic soda solution, containing 50 grammes NaOH in 100 c.c., and 170 c.c. of pure concentrated glycerin. This reagent is kept in a bottle closed with a rubber stopper.

2. *Dilute Sulphuric Acid.*—30 c.c. of pure concentrated sulphuric acid diluted with distilled water to 100 c.c.

[1] Goldmann, .*Chem. Zeit.*, 1888, xii. p. 183 ; xiv. p. 216 ; xx. p. 317 ; *Jour. Soc. Chem Ind.*, vii. (1888), pp. 238 and 348. Beal, *Jour. Amer. Chem. Soc.*, xvi. (1894), p. 673 ; *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 197.

[2] *Zeits. f. Anal. Chem.,* xviii. p. 68.

[3] For a full account, see Richmond, *Analyst*, xvii. (1892), p. 171.

3. *Decinormal Sulphuric Acid,* accurately standardized.

4. *Caustic Soda Solution* of approximately decinormal strength. A 10. c.c. pipetteful of this solution must be tinted with phenolphthalein and the strength determined by titration with the decinormal sulphuric acid.

5. *Phenolphthalein Solution.* (See p. 216.)

To determine the Reichert-Meissl value, a dry conical flask of 300 c.c. capacity is counterpoised on the balance. As nearly as possible 5 grms. of the oil or melted fat are dropped into the flask and the exact weight taken (in the case of a melted fat after becoming quite cold). 20 c.c. of the glycerol-soda are added, and the flask is heated over an Argand-Bunsen flame turned rather low. The liquid will foam, and to control this and hasten the operation the flask is frequently agitated. Heating and agitation are continued until practically all the water has been driven off, which will take about ten minutes ; saponification will then be complete, and the flask is withdrawn from the flame and the soap dissolved by adding 135 c.c. of cold water. The first portions of water should be added drop by drop, and the flask shaken between each addition to avoid violent foaming. When the soap is dissolved, 5 c.c. of the dilute sulphuric acid are added, a few small fragments of pumice are dropped in, and the liquid is distilled until 110 c.c. have been collected. The tube connecting the flask to the condenser should have a large bulb to arrest the splashings and return them to the flask. The condensing tube should be of glass, and the rate of distillation such that the above amount of distillate is collected in about thirty minutes.

The whole of the distillate, if clear, is mixed with about 0·5 c.c. of phenolphthalein solution, and as many 10 c.c. pipettefuls of the standard caustic soda solution are added as are required to produce a strong crimson coloration ; the liquid is then carefully titrated with decinormal sulphuric acid until the crimson colour is just discharged.

The distillate, if not clear, is passed through a dry ribbed filter, and 100 c.c. of the clear filtrate are titrated ; in this case, the volume of decinormal soda neutralized is increased by one-tenth.

A blank distillation must be made to determine the amount of decinormal soda required by the materials employed ; with a good quality of glycerin this will not exceed 0·5 c.c.

EXAMPLE.

5 grms. of blown rape oil gave 110 c.c. of distillate, which was filtered. 100 c.c. of the filtrate were mixed with 10 c.c. of standard caustic soda solution, and 4·76 c.c. of decinormal H_2SO_4 were required for neutralization.

10 c.c. of standard soda required,		9·78 c.c. $\frac{N}{10} H_2SO_4$
Deduct,		4·76 c.c.
Difference = volume of decinormal alkali required for 100 c.c. of distillate,		5·02
+ $\frac{1}{10}$th,		·50
∴ Volume required for 110 c.c.,		5·52
Deduct for blank experiment,		·40
Reichert-Meissl value (*volume of decinormal alkali required for 5 grammes of oil*),		5·12

*16

This process is used most extensively in the analysis of butter fat,[1] 5 grms. of which, when genuine, usually yield a distillate requiring from 24 to 34 c.c. of decinormal alkali. Results obtained with other oils are given in Table LXIII.

TABLE LXIII.

Description of Oil, etc.	Reichert Value = c.c. of N/10 Alkali required for 2·5 grms.	Reichert-Meissl Value = c.c. of N/10 Alkali required for 5 grms.
Olive oil,	0·3	0·45– 1·5
Hazel nut oil,	...	0·99
Arachis (earthnut) oil,	...	0·0 – 1·6
Castor oil,	1·4	1·1 – 4·0
Croton oil,	...	12·1 –13·6
Coconut oil,	3·5 – 3·7	6·7 – 8·4
Palm nut oil,	2·4	5·0 – 6·8
Palm oil,	0·5 – 0·8	0·7 – 1·9
Rape oil,	0·0 – 0·8	0·0 – 0·8
Curcas oil,	...	0·28– 0·55
Cottonseed oil,	0·3	0·95
Sesamé oil,	0·35 (2·2)	1·2
Maize oil,	0·33– 4·3	...
Linseed oil,	...	0·0 – 0·9
Poppyseed oil,	...	0·0 – 0·6
Sunflower oil,	...	0·5
Tallow,	0·25	1·0 – 1·2
Lard,	...	0·0 – 1·1
Horse fat,	0·3 – 0·4	1·6 – 2·1
Sperm oil,	1·3 – 1·4	...
Porpoise jaw oil (skimmed and strained),	47·8 –56·0	131·6
Porpoise jaw oil (unstrained),	2·1	...
Dolphin jaw oil (skimmed and strained),	65·9	...
Porpoise body oil,	11–12	46·9
Dolphin body oil,	5·6	...
Whale oil,	0·7 –12·5	...
Seal oil,	0·07– 0·22	...
Cod-liver oil,	0·2 (1·1–2·1)	0·1 – 0·4
Menhaden oil,	1·2	...
Wool fat (crude),	...	6·5
Blown East India rape oil,	...	5·26– 8·8
„ ravison oil,	...	5·43
„ cottonseed oil,	...	7·06

[1] The standard method adopted by a Joint Committee of the Government Laboratory and the Society of Public Analysts for the analysis of butter-fat is a modification known as the Reichert-Wollny Process. (See the *Analyst*, 1900, 309.)

It will be seen that the process is chiefly of value in the analysis of (besides butter fat) porpoise and dolphin oils and croton oil. It would not be of much service for the detection of blown oils, unless these were present in large quantity.

K.—ACETYLATION TEST (THE ACETYL VALUE).

The action of acetic anhydride (acetyl oxide) upon alcohols and hydroxylated fatty acids is applied in the analysis of lubricants both in the examination of unsaponifiable matter containing or suspected to contain wax alcohols, and also in the analysis of castor oil.

I. **Acetylation of Alcohols.**—When the alcohols are heated with acetic anhydride they are converted into acetates (esters), the hydrogen of their hydroxyl group or groups being replaced by acetyl, C_2H_3O. Thus, in the case of cetyl alcohol (from spermaceti) the following reaction takes place :—

$$\underset{\text{Cetyl alcohol}}{C_{16}H_{33}OH} + \underset{\text{Acetic anhydride}}{(C_2H_3O)_2O} = \underset{\text{Cetyl acetate}}{C_{16}H_{33}O.C_2H_3O} + \underset{\text{Acetic acid}}{C_2H_4O_2}$$
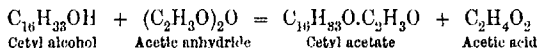
Glycerol, $C_3H_5(OH)_3$, is similarly converted into tri-acetin $C_3H_5(OC_2H_3O)_3$, but this reaction does not interest us here, since glycerol does not occur in the 'unsaponifiable matter.' Hydrocarbons are unacted upon. In the case of the monohydric alcohols, cholesterol, and phytosterol, the esters formed are crystalline bodies, insoluble in water, which can be washed free from acetic acid and weighed. The saponification values of these esters are characteristic, and afford a means of identifying the waxes, as well as a method of determining the proportion of a single known wax, such as sperm oil or wool fat, in a mixture containing hydrocarbons. The process is carried out as follows :—

A quantity of not less than 2–3 grms. of the unsaponifiable matter is boiled with acetic anhydride in a small flask under a reflux condenser for half an hour. If the *yield* of acetates is to be determined, the weight of the substance taken must be exactly known, and the flask must also be tared. 1 c.c. of acetic anhydride per grm. of substance is sufficient, but if the available weight of substance be small, 2 c.c. per grm. may be used in order to give a sufficient quantity of liquid to boil. If the unsaponifiable matter consist chiefly of alcohols, it will dissolve completely in the hot liquid ; but if a considerable proportion of hydrocarbons are present, they will float on the liquid, and may give rise to explosive ebullition ; in this case, a few small fragments of ignited pumice stone should be dropped into the flask.

The contents of the flask are next diluted with boiling water and heated over the steam-bath, with frequent agitation, for a few minutes, in order to convert the unchanged acetic anhydride into acetic acid, which dissolves in the water, and to allow the esters, together with hydrocarbons if present, to rise and float upon the surface as an oily layer. The hot liquid is next poured upon a wet filter, and if it be desired to ascertain the weight of the

acetylated product the flask is thoroughly rinsed on to the filter with small quantities of boiling water, until free from acetic acid ; it is then placed in the water-oven to dry. The oily liquid in the filter is thoroughly washed with boiling water until the washings are perfectly neutral, and the filter is then placed in a dry funnel over the flask in the water-oven until the acids have run through. The oil absorbed by the filter paper is (after cooling) rinsed into the flask with ether (or with boiling chloroform if myricyl alcohol is present), the solvent is evaporated off, and the residue is weighed constant. The saponification value is then determined in the usual way on 2·5 grms., or the whole quantity may be used if not exceeding 2·5 to 3 grms. in weight.

Table LXIV. contains the results obtained by treating in this way the unsaponifiable matter (mixed alcohols) from sperm oil, wool fat, beeswax, and carnauba wax ; also the results theoretically yielded by some alcohols known to occur in fats and waxes.

TABLE LXIV.—RESULTS OF THE ACETYLATION OF ALCOHOLS.

Alcohol.	Formula.	Formula of Acetate.	Yield of Acetate per 100 pts. of Alcohol (Theory).	Saponification Value of Acetate, per cent. (Theory).
Cetyl,	$C_{16}H_{33}OH$	$C_{16}H_{33}O.C_2H_3O$	117·35	19·76
Octadecyl,	$C_{18}H_{37}OH$	$C_{18}H_{37}O.C_2H_3O$	115·55	17·99
Ceryl,	$C_{27}H_{55}OH$	$C_{27}H_{55}O.C_2H_3O$	110·61	12·81
Myricyl,	$C_{30}H_{61}OH$	$C_{30}H_{61}O.C_2H_3O$	109·59	11·69
Cholesterol, Phytosterol,	$C_{26}H_{43}OH$	$C_{26}H_{43}O.C_2H_3O$	111·29	13·56

Unsaponifiable Matter (Mixed Alcohols, etc.), from	Yield of Mixed Acetates per cent. (Experiment).	Saponification Value of Mixed Acetates per cent. (Experiment).
Sperm oil,	115·71	18·55
Wool fat (crude),	112·21	16·06
„ (neutral),*	112·7	15·63
„ „	108·3 (?)	15·32
Beeswax.	106·46	9·84
„ (another sample),	107·62	10·25
Carnauba wax,	110·17	12·14
Cholesterol (pure),‡	...	13·49

* Lewkowitsch, *Jour. Soc. Chem. Ind.*, xi. (1892), p. 138.
•| *Ibid.*, xv. (1896), p. 14.   ‡ *Ibid.*, xi. (1892), p. 143.

The alcohols of sperm oil are unknown ; according to Lewkowitsch they belong for the most part, if not wholly, to the ethylene series. The alcohols of wool fat are also partly unknown, but cholesterol and isocholesterol occur in them to a large extent, and ceryl alcohol also is present. Myricyl alcohol is the chief part of the unsaponifiable matters from carnauba wax and beeswax ; in the latter, hydrocarbons occur to the extent of 15–17 per cent., which accounts for the low saponification value of the acetylated product. Cetyl palmitate is the chief constituent of spermaceti, in which octadecyl alcohol also occurs.

Analysis of Mixtures containing Sperm Oil or Wool Fat and Mineral Oil.

—(a) When a mixture containing sperm oil or wool fat and mineral oil is saponified, the unsaponifiable matter extracted from the soap solution by ether contains the whole of the mineral oil together with the mixed alcohols of the wax, and in order to determine the percentage of mineral oil directly, the alcohols must be separated. No satisfactory method of doing this has yet been proposed. Both ordinary alcohol and acetic anhydride, even in the cold, dissolve not only the wax alcohols but also some of the mineral oil, and therefore the methods described by Horn [1] and Lobry de Bruyn [2] are not trustworthy.

(b) The percentage of sperm oil in a mixture containing nothing else except mineral oil could easily be calculated, with approximate accuracy, from the saponification value of the mixture ; but when a second, perhaps unknown, fatty oil is present, this method is not available. Assuming that the third constituent of the mixture is not another wax such as wool fat, or a liver oil, containing much cholesterol, the problem can be solved by determining the percentage of total unsaponifiable matter, acetylating it, and determining the saponification value of the acetylated product. Taking the numbers for sperm oil given in the table above, and 38 as the percentage of mixed alcohols formed by the saponification, the percentages of mineral oil and sperm oil in the mixture can be calculated as follows :—

Let x = the percentage of total unsaponifiable matter yielded by the sample.

y = the percentage of KOH required for the saponification of the acetylated product.

Then, $\dfrac{x \times y \times 100}{18\cdot55 \times 115\cdot71}$ = the percentage of mixed alcohols (a) yielded by the sample.

$x - a$ = the percentage of mineral oil

$\dfrac{100\,a}{38}$ = the percentage of sperm oil.

[1] *Jour. Soc. Chem. Ind.*, vii. (1888), p. 696.
[2] *Ibid.*, xiii. (1894), p. 426.

To test the method, two mixtures of sperm oil and '885' pale mineral oil were prepared and analysed with the following results :—

1. *Mixture containing 2 parts sperm oil and 1 part mineral oil.*

Weight taken ; 5 grms.
Unsaponifiable matter obtained, 2·9706 grms. $= 59·41$ Per cent.

Saponification value of the } acetylated product, } 9·05 per cent.

$$\frac{59·41 \times 9·05 \times 100}{18·55 \times 115·76} \overset{\text{\textit{c}}}{=} 25·04$$

Mineral oil found, 34·37
„ taken, 33·33

2. *Mixture containing 2 parts mineral oil and 1 part sperm oil.*

Weight taken ; 5 grms.
Unsaponifiable matter obtained, 3·9892 grms. $= 79·78$ Per cent.

Saponification value of the } acetylated product, } 3·47 per cent.

$$\frac{79·78 \times 3·47 \times 100}{18·55 \times 115·76} = 12·89$$

Mineral oil found, 66·89
„ taken, 66·66

Buisine's process for determining hydrocarbons in beeswax, which consists of heating the wax with potash-lime to 250° C., whereby the wax alcohols are converted into fatty acids and soaps, from which the unchanged hydrocarbons can be extracted by means of ether,[1] would be applicable to a mixture of sperm oil and mineral oil, but not to a mixture containing wool fat or cholesterol, since the latter remains practically unchanged (see Lewkowitsch, *Jour. Soc. Chem. Ind.*, 1896, p. 14).

II. Acetylation of Hydroxylated Fatty Acids and Glycerides.

Determination of the Acetyl Value.—The action of acetic anhydride on hydroxylated fatty acids is similar to its action upon alcohols, the hydrogen of the alcoholic hydroxyl group or groups being replaced by acetyl. Thus :—

$$C_{17}H_{32}(OH)COOH + (C_2H_3O)_2O = C_{17}H_{32}(O.C_2H_3O)COOH + C_2H_4O_2$$

Ricinoleic acid   Acetic anhydride   Acetyl-ricinoleic acid   Acetic acid
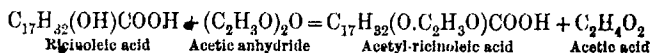
Benedikt and Ulzer, believing that those fatty acids which contain no alcoholic hydroxyl, such as stearic, oleic, and all the more commonly occurring fatty acids, are unacted on by acetic anhydride, proposed the following method for the valuation of castor oil :—

[1] See Lewkowitsch, *Chem. Technology, etc.*, 3rd edition, p. 380.

Benedikt's Method.—About 20 grms. of the insoluble fatty acids, prepared as directed on p. 238, are boiled with an equal volume of acetic anhydride for two hours in a flask connected to a reflux condenser. The contents of the flask are poured into a Jena glass beaker of 1 litre capacity and diluted with about 500 c.c. of boiling water; the beaker is then placed on a thin disc of asbestos millboard, and the liquid is boiled briskly for half an hour with a cover on the beaker. To prevent explosive ebullition, a slow current of carbon dioxide is conducted through the liquid by means of a piece of thermometer tube reaching nearly to the bottom of the beaker. The oil and water are allowed to separate, the aqueous liquid is siphoned off, and the oily layer is again boiled with water. After boiling in this way with three successive quantities of water, the oil is poured on to a wet filter and washed with boiling water until the washings are neutral. The filter containing the acetylated acids is then removed to a dry funnel, which is placed in the water-oven over a dry beaker and left until the acids have run through.

2·5 grms. of the dry acetylated acids thus prepared are weighed into a small flask, dissolved in about 10 c.c. of neutralized rectified alcohol, mixed with a few drops of phenolphthalein solution, and very carefully titrated with seminormal alcoholic potash added from a burette until the liquid is coloured faintly pink. The exact volume of potash solution used having been read off and recorded, about twice as much more is run into the flask from the burette, and the flask is then corked and boiled under an inverted condenser for one hour [1]; the excess of potash is then determined by titration with seminormal hydrochloric acid, exactly as in determining the saponification value. The potash solution is standardized with the same acid.

On the first neutralization with potash in the cold, the following reaction takes place :—

$$C_{17}H_{32}(O.C_2H_3O)COOH + KOH = C_{17}H_{32}(O.C_2H_3O)COOK + H_2O$$
<div align="center">Acetyl-ricinoleic acid   Potassium acetyl-ricinoleate</div>
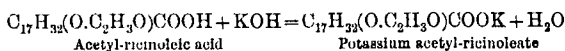
The percentage of potash required for this reaction was called by Benedikt the *acetyl acid value.*

By adding more potash and heating, saponification occurs, thus :—

$$C_{17}H_{32}(O.C_2H_3O)COOK + KOH = C_{17}H_{32}(OH)COOK + KC_2H_3O_2$$
<div align="center">Potassium acetyl-ricinoleate   Potassium ricinoleate   Potassium acetate</div>
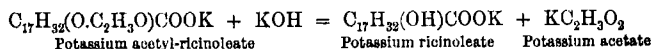
the percentage of potash required for this reaction is called the *acetyl value.*

EXAMPLE.

2·5 grms. of the acetylated fatty acids from a sample of castor oil required 13·22 c.c. N/2 KOH for neutralization. $13·22 \times 0·02807 = 0·3711$ grm. KOH required for 2·5 grms. = 14·84 grms. KOH for 100 grms.; therefore, the *acetyl acid value* was 14·84.

26·22 c.c. more N/2 KOH were added, and after boiling for one hour 13·41 c.c. of N/2 HCl were required for neutralization. Therefore, the acetic acid formed on saponification required $26·22 - 13·41 = 12·81$ c.c. N/2 KOH for neutralization, $= 12·81 \times 0·02807 = 0·3598$ grm. KOH for 2·5 grms. = 14·39 grms. KOH for 100 grms.; therefore, the *acetyl value* was 14·39.

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[1] A large excess of potash and long heating are necessary for the complete saponification of the acetylated acids.

The results in the following table were obtained by Benedikt and Ulzer :—

TABLE LXV.—ACETYL VALUES OF OILS (*Benedikt*).

Description of Oil.	Mixed Fatty Acids.	Acetylated Acids.	
	Acid Value (KOH required for neutralization), per cent.	Acetyl Acid Value, per cent.	Acetyl Value, per cent.
Arachis (earthnut),	19·88	19·33	0·34
Olive,	19·71	19·73	0·47
Rape,	18·25	17·85	0·63
Peach-kernel, .	20·25	19·60	0·64
Hempseed,	19·94	19·68	0·75
Walnut, .	20·48	19·80	0·76
Croton,	20·10	19·57	0·85
Linseed, .	20·13	19·66	0·85
Sesamé, .	20·04	19·20	1·15
Poppyseed,	20·06	19·41	1·31
Cottonseed,	19·98	19·57	1·66
Grapeseed (*Horn*), .	...	...	14·45
Castor, .	17·74	14·28	15·34
'Blown oil,' .	...	18·45	6·22

The following results were obtained by Archbutt :—

Description of Oil.	Acetyl Value of the Insoluble Fatty Acids by Benedikt's Process, per cent.
Castor oil,	14·95–15·08
Blown East India rape oil,	5·68
Blown ravison oil,	5·37
Blown cottonseed oil, .	6·96

Thus, castor oil is sharply distinguished from the other natural oils (except grapeseed oil) by its high acetyl value, less sharply from blown oil, though 10 per cent. of the above sample of blown oil (Table LXV.) would lower the acetyl value of castor oil from 15·34 to 14·43 per cent.

Lewkowitsch[1] has shown that Benedikt's method of determining the acetyl values of oils is subject to an important error, and that pure stearic, oleic, and other fatty acids which contain no alcoholic hydroxyl

[1] *Proc. Chem. Soc.* (1890), pp. 72, 91 ; *Jour. Soc. Chem. Ind.*, ix. (1890), p. 660.

may, nevertheless, give considerable acetyl values when treated by Benedikt's process. This he explains by stating that the fatty *acids* when boiled with a large excess of acetic anhydride are converted more or less completely into *anhydrides*, as shown by the following equation :—

$$2C_{15}H_{31}COOH + (C_2H_3O)_2O = (C_{15}H_{31}CO)_2O + 2CH_3COOH$$

<div align="center">Palmitic acid   Acetic anhydride   Palmitic anhydride   Acetic acid</div>
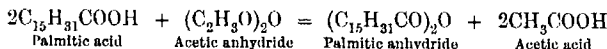
When the acetylated product is boiled with water, the greater part of the anhydride is reconverted into acid,

$$(C_{15}H_{31}CO)_2O + H_2O = 2C_{15}H_{31}COOH,$$
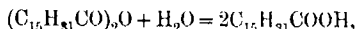
but a variable proportion remains unchanged, and does not combine with potash *in the cold* ; thus the acetyl acid value is too low. On *boiling* with potash, however, the anhydride readily undergoes hydrolysis, and, by neutralizing potash, causes a fictitious acetyl value to be obtained. On this account, the acetyl values obtained by other observers have not always agreed with Benedikt's numbers.

In order to avoid the error due to the formation of fatty anhydrides, Lewkowitsch has proposed to determine the acetyl value by distilling off and determining in the distillate the acetic acid formed by saponi-fication of the acetylated fatty acids. He has since proposed to acetylate the glycerides themselves.

Lewkowitsch's Method.—10–20 grms. of the oil or fat, from which free fatty acids, if exceeding 5 per cent. in amount, should be first removed as directed on p. 218 (III or V), are boiled for two hours with an equal volume of acetic anhydride and then washed by boiling with three successive half litres of water, for half an hour each time, as in washing the acetylated fatty acids in Benedikt's process (p. 247). The acetylated glycerides are further washed on a wet filter until every trace of acid is removed, and finally dried in the water-oven.

5 grms. of the acetylated oil are saponified by boiling for half an hour, under a reflux condenser, with 70 c.c. of seminormal alcoholic potash. The soap solution is then rinsed with neutral alcohol into a porcelain basin and evaporated over the steam-bath until the alcohol is expelled. The soap is dissolved in boiling water, rinsed into a 12-oz. flask, and decomposed by adding *exactly* the volume (ascertained by a separate experiment) of semi-normal hydrochloric acid or sulphuric acid necessary to neutralize the 70 c.c. of standard potash. The flask is closed by a cork carrying a long glass tube. The fatty acids will melt and form a clear oily layer on the surface of the liquid, and the acetic acid, together with any soluble fatty acid present, will dissolve in the aqueous liquid. (In order to facilitate the separation of the fatty acids, a little mineral acid may be added, which must be carefully measured and allowed for in the subsequent titration.) When cold, the aqueous liquid is poured through a wet filter and the fatty acids are thoroughly washed with hot well-boiled distilled water free from CO_2 until the soluble acid is removed. This part of the process resembles the determination of the Hehner value (p. 237). The filtrate, which must be perfectly bright, is then titrated with decinormal alkali, using phenol-phthalein as indicator, and, from the result, the number of grms. of potash required to neutralize the acetic acid formed on saponifying 100 grms. of the acetylated oil is calculated.

TABLE LXVI.—ACETYL VALUES OF OILS (*Lewkowitsch*).

Class.	Description of Acetylated Oil.	True Acetyl Value. Per cent.
Vegetable Non-drying Oils and Fats.	Olive oil, ...	1·06
	Arachis (earthnut) oil, . .	0·91
	Castor oil, ...	14·67–15 05
	Japan wax, ...	1·73 – 2·66
	Coconut oil, ...	0·09 – 1·23
	Palm nut oil, ...	0·19 – 0·84
	Palm oil, ...	1·60
Vegetable Semi-drying Oils.	Rape oil, ...	1·47
	Cottonseed oil, . . .	0·76 – 1·80
	Maize oil, ...	0·58
Vegetable Drying Oil.	Linseed oil, . . .	0·40
Animal Oils and Fats.	Neatsfoot oil, . . .	0·22
	Lard oil, ...	0·26
	Horsefoot oil, . . .	0·94
	Animal oil, ...	1·85
	Tallow, ...	0·24 – 0·86
	Bone fat, ...	1·13
Marine Animal Oils and Fluid Waxes.	Sperm oils (Southern and Arctic),	0·41 – 0·64
	Seal oil, ...	1·52
	Cod-liver oil, . . .	0·11
	Fish oil (containing coast cod oil, etc.). . . .	3·27
	Skate liver oil, . . .	1·01
	Shark liver oil, . . .	0·90
	Japan fish oil, . . .	1·16
Waxes (solid)	Wool wax, ...	2·33
	Spermaceti, . . .	0·26
	Beeswax, ...	1·52
	Carnauba wax, . . .	5·52
Blown Oils.	Blown East India rape oil (·962),	4·66
	Blown ravison oil (·968), .	5·25
	Blown cottonseed oil (·979),	6·42

Acetyl values determined by the foregoing method include the potash required to neutralize the soluble fatty acids present in the oil or fat; the true acetyl values are obtained by deducting this. Lewkowitsch has published a number of determinations, from which those in Table LXVI. are selected.

Lewkowitsch, who has made a very complete investigation into the meaning of the acetyl value (*Analyst*, 1899, p. 319) has shown that it must not be looked upon as a constant, except in the case of castor oil, since it measures, besides hydroxylated acids, the following substances which may occur in variable proportions in oils and fats, viz.:—free alcohols (including cholesterol and phytosterol), oxidized and unknown fatty acids occurring in blown oils, also mono- and diglycerides resulting from natural hydrolysis of triglycerides in oils and fats which have been kept. Oils and fats which have become rancid by keeping possess higher acetyl values than when in the fresh condition. These considerations show the necessity of taking precautions to prevent oxidation of oils or fatty acids obtained from them, previous to the determination of the acetyl value.

L.—THE IODINE VALUE.

I. Meaning and Use of this Value.

The iodine or Hübl value of a substance is the percentage of iodine absorbed from solution under definite conditions prescribed by Hübl in 1884.[1] The value of the test depends upon the fact that oils, fats, and allied bodies are mixtures, in very variable proportions, of glycerides of saturated and unsaturated fatty acids, and that whilst the latter readily unite with the halogens and form addition products, the former do not. By bringing the oil and the halogen together in solution under conditions which reduce substitution to a minimum, it is found that the amount of halogen absorbed by each kind of fat and oil is very characteristic, and affords one of the most reliable means we possess of distinguishing one kind of oil from another and of determining their proportion in mixtures. The test is most generally useful in the analysis of fixed oils and fats, but it has a limited value in the identification of mineral lubricating oil, vaseline, and paraffin wax. The halogen at first used was bromine. Allen published details of a bromine process in 1881,[2] and an improved process was described by Mills in 1883 and 1884;[3] but Hübl's iodine process has gradually superseded these. It has been the subject of numerous modifications, but the only one of permanent value is that due to Wijs,[4] which has greatly simplified and improved the Hübl

[1] *Jour. Soc. Chem. Ind.*, iii. (1884), p. 641.
[2] *Analyst*, vi. (1881), pp. 177 and 215.
[3] *Jour. Soc. Chem. Ind.*, ii. (1883), p. 435; iii. (1884), p. 366.
[4] *Berichte*, 1898, p. 50.

process. We shall describe both processes, but the latter (Wijs's) is the one which recommends itself for use.

11. Determination of the Iodine Value.

(a) **Hübl's Process.** —The following solutions are required :—

Iodine Solution.—This is a solution, in ethyl alcohol, of iod·ne and mercuric chloride, in the proportion of at least one molecule of mercuric chloride to every molecule of iodine. The presence of mercuric chloride renders the absorption of the halogen by the fat more rapid and complete. and is essential for the attainment of constant results.[1]

In preparing the solution according to Hubl's directions, 1 litre of pure 9£ per cent. alcohol is divided into two equal parts ; in one, 25 grms. of iodine are dissolved (heating hastens solution), and in the other, 30 grms. of powdered mercuric chloride (easily soluble in the cold) ; the two solutions are then mixed. The solution must be kept in a well-stoppered bottle in a dark, cool cupboard. At first the strength is about one-fifth normal, but the free iodine gradually and continually diminishes, at first rapidly and afterwards more slowly.[2] The solution, when freshly prepared, should be allowed to stand for from six to twelve hours before use. Every time it is used it must be standardized. Owing to the continual diminution of strength a solution many weeks old can no longer be relied upon to give the maximum iodine absorption with substances of high iodine value, and, as the action of the iodine on the alcohol is much less rapid in the absence of mercuric chloride, it is far better to keep the solutions of iodine and mercuric chloride in separate bottles and to mix them only a few hours before being required for use.

Decinormal Thiosulphate Solution—This may be prepared by dissolving 12·4125 grms. of pure dry sodium thiosulphate crystals ($Na_2S_2O_3.5H_2O$) in water and diluting to 500 c.c. at 60° F. The recrystallized salt, as purchased is almost chemically pure, but generally damp ; the crystals merely require crushing, drying by moderate pressure between folds of blotting-paper, and preserving in a well-stoppered bottle. If the above stated quantity of the dried salt be made up to exactly 500 c.c., the solution will be so nearly correct that for ordinary work it is not necessary to standardize it ; and if kept in the dark, it alters in strength very slowly. But it is easier and more satisfactory to prepare an approximately decinormal solution, by dissolving 12·5 grms. of the undried crystals, and to standardize this by means of pure potassium bichromate.

The pure bichromate is prepared by recrystallizing the commercial salt a few times, and is obtained in the form of fine granular crystals by stirring and rapidly cooling a hot saturated solution. The crystals are filtered by

[1] According to Wijs (*Jour. Soc. Chem. Ind.*, 1898, 698), iodine monochloride is first formed, as shown by Ephraim, $HgCl_2 + 4I = HgI_2 + 2ICl$, but this reacts with the water of the alcohol to form hypoiodous acid, which is the active agent thus :—$ICl + H_2O = HCl + HIO$. Lewkowitsch prefers to assume that ICl is added on directly.

[2] Owing to the fact that the hypoiodous acid gradually oxidizes the alcohol to aldehyde, thus :—$C_2H_6O + 2HIO = C_2H_4O + 2H_2O + I_2$. In this reaction, 2HIO (two molecules) liberate I_2, whereas one molecule of undecomposed HIO liberates I in the titration, thus :—$HCl + HIO + KI = KCl + H_2O + I_2$.

suction, dried in the air-oven at 150°–200° C., and kept in a stoppered bottle.

For standardizing the thiosulphate, an accurate 1 per cent. solution of the bichromate is prepared, and is kept in a well-stoppered bottle. 10 c.c. of this solution are measured into an 8-oz. stoppered bottle and diluted with about 4 oz. of cold distilled water. 20 c.c. of a 10 per cent. solution of pure potassium iodide (free from iodate) are added, and about 10 c.c. of dilute sulphuric acid (1 vol. of strong acid to 3 vols. of water). This acid liberates exactly 0·2584 grm. iodine, equivalent to about 20·4 c.c. of decinormal thiosulphate. The thiosulphate solution is then added from a burette *in drops*,[1] with continual agitation of the liquid, until the colour of the free iodine has nearly disappeared. Starch solution is then added, and the titration is finished very slowly, by adding the thiosulphate at first two drops and then one drop at a time and allowing plenty of time between each addition, as the final destruction of the blue iodide of starch takes place slowly and it is easy to overshoot the mark. The colour of the solution is not bleached, but changes to the pale bluish-green of chromium chloride. If x be the number of c.c. used, then 1 c.c. of thiosulphate solution is equivalent to $\dfrac{0·2584}{x}$ grm. of iodine.

An alternative, and in some respects preferable, method of standardizing the decinormal thiosulphate solution is by means of decinormal permanganate solution. 100 c.c. of distilled water, 10 c.c. of dilute sulphuric acid (1 vol. of acid to 3 vols. of water), and 20 c.c. of a 10 per cent. solution of pure potassium iodide, are well mixed in a stoppered bottle. 20 c.c. of decinormal permanganate solution are then added and the liberated iodine titrated with the thiosulphate solution. 20 c.c. of decinormal permanganate solution of correct strength liberate 0·2539 grm. of iodine.

Potassium Iodide Solution.—This is a 10 per cent. aqueous solution of the pure salt free from iodate. It becomes slightly yellow on keeping, owing to liberation of iodine, but may be bleached by adding a drop or two of thiosulphate.

Starch Solution.—About 1 grm. of pure arrowroot starch is rubbed to a smooth cream with a few drops of water and poured into an 8-oz. conical beaker. The beaker is nearly filled with boiling water, immediately placed over the naked flame of an Argand-Bunsen for a few moments, and allowed to boil up. It is then covered and left to stand over night, and the clear liquid is decanted for use. If required for use immediately, the hot liquid may be filtered.

Methylated Chloroform.—This must be proved to absorb no iodine. Place 10 c.c. and 20 c.c. in two stoppered bottles. Add to each, 10 c.c. of iodine solution, and stopper the bottles tightly, after moistening each stopper with a drop of potassium iodide solution. Place the bottles in a dark cupboard for several hours, and then titrate the free iodine in each; if the volume of thiosulphate used is the same for both, the chloroform is fit for use.

To determine the iodine value, as much of the substance is weighed 'n a very small counterpoised beaker as will absorb about 0·3 grm. of iodine, or a trifle more. It is dissolved in chloroform[2] and rinsed into a dry 8-oz.

[1] If the thiosulphate be added more rapidly, an excessive quantity is required.
[2] In testing a substance which is insoluble in chloroform but soluble in alcohol, either the substance is transferred to the bottle in a dry state, or it is dissolved in 10 c.c. of absolute alcohol and exactly the same volume of absolute alcohol is added to the blank quantity.

stoppered bottle, about 10 c.c. of chloroform being used altogether. About the same volume of chloroform is then poured into another similar bottle. Both bottles must have very well fitted stoppers.

The approximate strength of the iodine solution having been ascertained by titrating 10 c.c. with the standard thiosulphate, as much is measured into each bottle as will contain at least 0·6 grm. of iodine. If, after mixing, the contents of the bottle containing the substance be not clear, more chloroform is added, the same extra volume being added to the blank quantity. The bottles are then tightly stoppered, each stopper being first moistened with a drop of strong potassium iodide solution to make a more effective seal, and are placed in a cool, dark cupboard for not less than six, and not more than about eighteen, hours. It is convenient to commence the experiment late in the afternoon and titrate the first thing next morning.

Before commencing to titrate, each bottle, in warm weather, is first cooled by running some cold water over it, so as to produce a slight reduction of pressure inside, and a few drops of potassium iodide solution are poured round the stopper, which, on opening the bottle, are drawn in, rinsing the neck and stopper. 20 c.c. of potassium iodide solution are then poured into the bottle, and cold distilled water is added until the bottle is about two-thirds full. Part of the iodine will now be in the aqueous liquid, and part in the chloroform solution which settles to the bottom. The standard thiosulphate solution is next run in, at first rapidly and afterwards more slowly, with constant agitation, until the free iodine has nearly all disappeared, and then the starch solution is added and the titration is finished drop by drop, vigorously shaking the closed bottle between each drop, until the blue colour is destroyed. The difference between the volumes of thiosulphate solution used for the blank quantity and for the sample is calculated to iodine, and, when divided by the weight of substance taken and multiplied by 100, gives the iodine value.

EXAMPLE.

It was required to determine the iodine value of a sample of olive oil. 10 c.c. of iodine solution, rather old, required 17·2 c.c. of decinormal thiosulphate solution, equivalent to 0·217 grm. iodine ; therefore, a 30 c.c. pipetteful would contain about 0·65 grm. iodine. Now olive oil, when genuine, absorbs about 80 per cent. of iodine ; therefore, weighed out ·4 grm. In titrating, the volumes of thiosulphate solution used were,

For the blank quantity,	.	.	50·80 c.c.
For the test quantity,	.	.	24·30 c.c.
Difference,	.	.	26·50 c.c.

c.c. of the thiosulphate used was equivalent to 0·01261 grm. iodine ; therefore, 26·50 c.c. were equivalent to 0·33416 grm. Therefore, 0·4 grm. of the oil absorbed 0·33416 grm. iodine, and 100 grms. would absorb $0·33416 \div ·4 \times 100 = 83·54$, which is the iodine value of the sample.

For the attainment of uniformly reliable and concordant results by this process, about double as much iodine should be added as the substance can absorb. The iodine solution must not be too weak, otherwise the maximum iodine absorption is not obtained with oils of high iodine value. The digestion with iodine must not be continued for too short a time, nor unduly prolonged ; standing over night (about eighteen hours) is sufficient in all cases. Although these precautions are more necessary when dealing with substances

TABLE LXVII.—IODINE VALUES OF FIXED OILS, FATS, AND WAXES, AND THEIR MIXED FATTY ACIDS.

Class.	Name of Oil, etc.	Iodine Values. Iodine absorbed by 100 Parts.	
		Of Oil, Fat, etc.	Of Mixed Fatty Acids.
Vegetable Non-drying Oils and Fats.	Olive oil, .	76·2–91·7 (rarely exceeds 85)	86 – 90·2
	Olive kernel oil,	87 – 88	..
	Hazel nut oil, .	83 – 90	90·1– 90·6
	Ben oil, .	72 –113	..
	Arachis (earthnut) oil, .	83·3–105	95·5–103·4
	Castor oil,	81·4– 90 6	86·5– 88·5
	Japan wax, .	4·2 - 15·1	..
	Coconut oil,	8·3– 10	8·5– 9·5
	Palm nut oil, .	10 – 17·5	12
	Palm oil, .	53 – 57·4	53·5
	Cottonseed stearin, .	88·5–104	94·5
Vegetable Semi-drying Oils.	Rape oil, .	94·1–105·6	96·3–105·6
	Ravison oil, .	109 –122	126
	Mustard oil (white),	92·1–103	94·7 106·2
	Mustard oil (black), .	96 –122·3	109·5–126·5
	Curcas oil, .	98·3 100·9	105
	Cottonseed oil, .	100·9–116·9	111 –115·7
	Sesamé oil, .	102·5–115	109 –112
	Brazil nut oil, .	90·6–106·2	108
	Beech nut oil, .	111 120	114
	Maize oil, .	111·2–130·8	113 –125
	Cameline oil, .	135·3 -142·4	137
Vegetable Drying Oils.	Linseed oil, .	160 –201·8	178·5–209·8
	Hempseed oil, .	140·5–157·5	122 –141
	Poppyseed oil, .	132·6–157·5	116·5–139
	Walnut oil, .	132·1–151·7	150
	Nigerseed oil, .	126·6–133·8	147·5
	Sunflower oil, .	120·2–135	124 –134
Animal Oils and Fats.	Neatsfoot oil, .	66·8– 72·9	62 – 77
	Lard oil, .	67 – 88	..
	Horsefoot oil, .	73·7– 90·3	72·9– 78·7
	Tallow oil ('animal oil '), .	55·5– 60	55 – 57
	Tallow (beef, mutton, and home refined), .	32·7– 49·3	26 – 41·3
	Bone fat, .	46·3– 55·8	55·7– 57·4
	Lard, .	49·9– 76·9	64
	Horse fat, .	71·4– 86·3	84 – 87·1
Marine Animal Oils and Fluid Waxes.	Sperm oils (Southern and Arctic), .	67·1– 90·1	82·2– 88·1
	Porpoise jaw oil, strained from solid fat,	21·5– 49·6	..
	Porpoise jaw oil, unstrained,	77	..
	Dolphin jaw oil, strained from solid fat,	38	..
	Porpoise body oil, .	88 –119	..
	Dolphin body oil, .	99·5–126·9	..
	Whale oil, .	110 –136	130·3–132
	Seal oil, .	127 –162·6	..
	Cod liver oil, .	135 –181·3	130·5–170
	Other fish liver oils, .	90 –191·1	..
	Menhaden oil, .	139·2–172·6	..
	Sardine (including Japan fish) oil, .	100·0–193·2	..
Waxes (solid).	Wool fat, .	25 – 41	9 – 17
	Spermaceti (if free from sperm oil),	nil.	..
	Beeswax, .	7·9– 11	..
	Carnauba wax, .	13·5	..

TABLE LXVIII.—IODINE VALUES OF MISCELLANEOUS SUBSTANCES.

Class	Description.	Iodine Value = Iodine absorbed by 100 parts.
Blown Oils.	Blown rape oil, ...	47 – 73
	Blown cottonseed oil, . .	56 – 66
Alcohols.	Alcohols from sperm oil, . .	59·5– 69·3
	Alcohols from wool fat, . .	35 – 40
	Cholesterol and phytosterol, .	67·3 68·1
Resins.	Colophony, ...	160 –219 *
Solid Hydrocarbons.	Paraffin wax, ...	3·9– 4·0
	Ozokerite, ...	4·5– 4·9
	Vaseline (Chesebrough Co.), .	8·6
American Lubricating Oils.	Pale '885,' . . .	12·52
	'Red' engine oil, . .	16·06
	Dark medium machinery oil, .	14·15
	Dark cylinder oil, . .	15·62
Russian Lubricating Oil.	'Ragosine' oil No. 1, . .	7·19
Shale Oil.	Scotch shale oil, '890,' . .	22·99
	Rosin oil, ...	43–48

* Wijs's solution, two hours' contact (see Lewkowitsch, *Oils, Fats, etc.*, vol. i. p. 390).

of high than of low iodine value, it is desirable to adopt the same method of working in all cases.

The chemical reactions taking place in this process have been fully discussed in papers by Schweitzer and Lungwitz,[1] Ephraim,[2] Waller,[3] Wijs,[4] and Lewkowitsch[5]; for practical purposes it may be assumed that ICl is added on to the unsaturated carbon atoms.

[1] *Jour. Soc. Chem. Ind.*, xiv. (1895), pp. 130 and 1030.
[2] *Analyst*, xx. (1895), p. 176.   [3] *Ibid.*, p. 280.
[4] *Jour. Soc. Chem. Ind.*, 1898, p. 698.
[5] *Analyst*, 1899, p. 257.

(*b*) **Wijs's Process.**—Wijs has replaced Hübl's reagent by a solution of iodine monochloride in acetic acid.

The reagent is prepared by dissolving 13 grms. of iodine in 1 litre of pure glacial acetic acid, determining the titre of the solution, and then passing into it a current of chlorine (free from hydrochloric acid) until the titre is nearly but not more than doubled. With a little practice the point can be judged with fair accuracy by observing the change in colour from very dark brown to a rich orange. The acetic acid used must be proved to have no reducing action on permanganate. The solution thus obtained has the following advantages over the Hübl solution : it is comparatively stable, and will keep for six months without serious loss of strength ; the time of contact necessary for complete iodine absorption to take place is shortened to an hour or less (in the case of non-drying oils, a few minutes suffice).

To determine the iodine value with this solution, as much of the substance as will absorb about 0·325 grm. of iodine is dissolved in 10 c.c. of chloroform in a stoppered 8-oz. bottle, mixed with 25 c.c. of the Wijs solution (containing about 0·65 grm. of iodine) and allowed to stand fifteen minutes for non-drying oils (olive), thirty minutes for semi-drying oils (rape), sixty minutes for drying oils (linseed). 20 c.c. of potassium iodide solution are then added, followed by about 100 c.c. of distilled water, and the titration is proceeded with in the manner described on p. 254. There is no need to make a blank test, occasional titration of the Wijs solution being sufficient. Iodine values determined by this method agree closely enough for practical purposes with those determined by the Hübl method, when the latter is properly carried out, and as the method is much simpler it will naturally be preferred.

M.—HEHNER'S BROMINE THERMAL TEST.

Hehner and Mitchell have devised a very useful thermal method for the examination of oils. Hehner showed[1] that when liquid bromine is added to an oil or fat dissolved in chloroform or carbon tetrachloride, instantaneous combination occurs, accompanied by considerable evolution of heat, and in conjunction with Mitchell he subsequently discovered that the heat evolved, measured by the rise of temperature under fixed conditions, bears a nearly constant ratio to the iodine value ; that, in fact, the iodine value, which by Hübl's process takes several hours to determine and involves the use of a special reagent not always ready, can be ascertained with considerable accuracy in a few minutes by measuring the thermometric rise with bromine and multiplying the result by a constant.

Since iodine values can now be determined so rapidly by the Wijs process, the bromine thermal test has to a large extent lost its usefulness ; but it may still be employed with advantage as a sorting test,

LUBRICATION AND LUBRICANTS.

where a large number of samples have to be examined in a short time.

The following apparatus and reagents are required :—

A vacuum jacketed-tube,[1] measuring internally 3½ inches in length × ⅞ inch in diameter.

A Centigrade thermometer, divided in fifths of a degree from, say, 0° to 50°.

A 1 c.c. pipette, having a short soda-lime tube fixed by a cork to the upper end, with a flexible tube for mouthpiece.

Liquid bromine, and

Methylated chloroform.

The Process.—The vacuum-jacketed tube is suspended from one arm of the balance by means of a stiff platinum wire loop (fig. 72), a counterpoise made from a piece of thick sheet lead, being placed in the other pan. By opening the side door of the balance case, the oil or fat can be dropped into the tube and the exact weight easily and quickly adjusted. The tube is then slipped out of the wire loop and fixed firmly, by means of the short stem, in a suitable stand, and 10 c.c. of chloroform are measured into it from a pipette. The temperature of the bromine having been ascertained to the nearest 0·1 deg., by stirring with the thermometer, the same thermometer, freed from adhering bromine, is immersed in the chloroformic solution of the substance, which is brought to exactly the same temperature as the bromine, either by warming the outer tube by the hand or cooling it by immersion in cold water. This adjustment takes place slowly, as the heat can only be transmitted by radiation. Immediately the temperature is correctly adjusted, 1 c.c. of the bromine is withdrawn from the bottle (by means of a pipette, provided at its upper end with a short soda-lime tube and a flexible mouthpiece) and added to the chloroform solution, which is rapidly stirred with the thermometer until the mercury has risen to the highest point and begun to fall again. As this takes place in about fifteen seconds, close observation of the mercury is necessary. The difference between the initial and final temperatures is the rise of temperature.
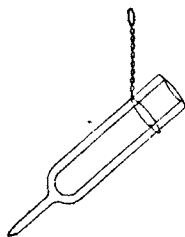
FIG. 72.—Vacuum Jacketed Tube.

It is desirable to vary the quantity of substance taken, according to the amount of heat developed. Of olive and rape oils,1 grm. is a suitable quantity ; of tallow or any other fat composed mainly of saturated glycerides, 2 grms. may be used ; but of linseed oil, which reacts very violently with bromine, 0·5 grm. is sufficient. 10 c.c. of chloroform and 1 c.c. of bromine are used in all cases. The rise of temperature when 2 grms. are used is divided by 2, and when 0·5 grm. is used is multiplied by 2. The result, expressed by the symbol β, may be called the *bromine thermal value.*

The numerical value of the constant or factor for converting the bromine thermal values into iodine values depends upon the heat capacity of the particular tube and thermometer used. Hehner and Mitchell found it to be about 5·5, Jenkins[2] 5·7, Archbutt[3]

[1] Obtainable from Messrs. Baird & Tatlock.

[2] *Jour. Soc. Chem. Ind.*, xvi. (1897), p. 193.

[3] *Ibid.*, p. 309.

TABLE LXIX.

Experiment.	Thermal Value (β). °C.		
	Bromine as Purchased.	Bromine saturated with Water.	Anhydrous Bromine.
1	20·4	20·2	20·1
2	20·3	20·4	20·2
3	20·1	...	...
4	20·2	...	...
Mean,	20·25	20·3	20·15

TABLE LXX.

1. Tallow. 7 samples (2 grms. used; the rise of temperature ÷ 2 = β).

Description.	Bromine Thermal Value (β)	$\beta \times 6 \cdot 2$	Hübl Iodine Value.
American beef, .	6·1	37·8	39·1
Home refined, .	6 7	41·5	41·3
"	6·7	41·5	41·8
"	7·05	43·7	44 3
"	7·2	44·0	44·9
Australian mutton, .	7·55	46·8	46·3
Home refined, .	8·9	55·2	53·5

3. Rape Oil. 11 samples (1 grm used; the rise of temperature = β).

Description.	Bromine Thermal Value (β)	$\beta \times 5 \cdot 92$	Hübl Iodine Value.
Stettin, .	17·0	100·6	99·6
Unknown,	17 35	102·7	102·7
"	17·4	103·0	103·3
"	17·3	102·4	103·1
"	17·7	104·8	105·7
"	17·8	105·4	104·8
"	17·9	105·9	106·2
"	18·25	108·0	108·1
"	18·6	110·1	109·4
Black Sea,	19·1	113·1	113·5
"	20·3	120·2	121·7

2. Olive Oil. 10 samples (1 grm. used; the rise of temperature = β).

Description.	Bromine Thermal Value (β).	$\beta \times 5 \cdot 7$	Hübl Iodine Value.
Unknown,	13·55	77·2	78·7
"	13·8	78·7	78·9
Malaga, .	13 8	78·7	79·3
"	14·2	80·0	78·4
Unknown,	14·2	80·9	81·4
"	14·35	81·8	81·4
Gallipoli,	14·4	82·1	82·0
Unknown,	14·45	82·4	84·2
Gallipoli,	14·5	82·6	82·5
"	14·5	82·6	82·1

4. Raw Linseed Oil. 10 samples (0·5 grm. used; the rise of temperature ×2 = β).

Description.	Bromine Thermal Value (β).	$\beta \times 6 \cdot 0$.	Hübl Iodine Value.
Old sample, .	28·5	171·0	167·1
Unknown, .	28·8	172·9	177·0
American (?), .	29·6	177·6	177·0
Unknown, .	29·7	178·2	177·8
Calcutta,	29 8	178·8	178·7
"	30·45	182·7	183·3
"	31·35	188·1	188·5
Baltic,	31·4	188·4	188·8
"	31·75	190·5	158·8
"	32·5	195·0	192·5

from 5·7 to 6·2, according to the nature of the oil. Each operator, in a test of this kind, must of necessity work out his own factors, by making comparative determinations of the iodine values and the bromine thermal values of about half a dozen genuine samples of each description of oil which he wishes to use the method for.

The results of consecutive experiments made with the same sample of oil are remarkably concordant, the extreme difference usually observed being 0·3° C. Duplicate experiments, made at intervals of several days, usually agree within 0·1° C. Bromine as purchased, the same fully saturated with water, and the same dehydrated by shaking with strong sulphuric acid and distilling, gave practically the same results, as the figures in Table LXIX., obtained with the same sample of rape oil, show.

The results of experiments with four descriptions of oil are given in Table LXX., and it will be seen that the agreement between the observed and the calculated iodine values is generally very satisfactory. Thus, with the seven samples of tallow, the maximum difference is 1·7 ; in the case of the olive oils, it is 2·5 ; eleven samples of rape oil gave a maximum difference of 1·5 ; and the agreement in the case of raw linseed oil is nearly as good. The greatest difference observed in testing ten samples of the latter oil was 4·2, but if we omit the first two samples the difference does not exceed 2·5. These results prove that the bromine thermal test is a valuable auxiliary method for the valuation of oils, which, in laboratories where a large number of oils of the same kind have to be examined, may save a great deal of time and labour.

N.—MAUMENÉ'S THERMAL TEST.

All the fixed oils react with strong sulphuric acid with evolution of heat, which is least in the case of the non-drying and greatest in that of the drying oils. In Maumené's test, 50 grms. of the oil are stirred in a beaker with 10 c.c. of strong sulphuric acid, both at the same initial temperature, and the rise of temperature is read off. This varies from about 40° C. with olive oil to about 130° C. with linseed oil ; and as the limits of variation with different pure samples of each oil are not wide, the test, when conducted with due care, is a valuable means of distinguishing one oil from another and of detecting adulteration.

The attainment of uniform results by this test depends upon the employment of identical conditions, especially as regards the strength of the sulphuric acid used. The following results by Archbutt[1] show the effect of varying the strength of the acid, all other conditions remaining the same.

[1] *Jour. Soc. Chem. Ind.*, v. (1886) p. 303.

TABLE LXXI.

Description of Oil.	Rise of Temperature (° C.) with Acid containing per cent. of H_2SO_4.						
	97·38	96·71	95·72	94·72	93·75	92·73	91·85
Olive oil, pure, .	42·7	42	39	36·5	34·5	31	28·6
Olive oil, impure, .	48·5	47·3	44	40·5	38·7	35·5	32·5
Rape oil, pure, .	62·5	61	58	54	50·3	47	41·7

As the temperature rises more slowly the weaker the acid, it is advisable to use an acid containing not less than 97 per cent. of H_2SO_4; and the strength must be ascertained by analysis, since the specific gravity of sulphuric acid reaches the maximum at 97·7 per cent., and then diminishes, so that acids of 95·6 per cent. and 99·2 per cent. strength have the same specific gravity (*Lunge* and *Naef*). The method of working which we recommend involves the use of the following reagent and apparatus : --

Sulphuric Acid (97% H_2SO_4); prepared as follows :-- The contents of an unopened Winchester quart bottle of pure sulphuric acid are well mixed ; about 6 c.c. are then taken out with a dry pipette, quickly delivered into a dry weighing bottle, which is stoppered and the exact weight taken. The acid is then carefully diluted with cold water, made up to exactly 500 c.c. at the temperature of the laboratory, and well mixed. 100 c.c. of the diluted acid are next measured with a pipette and delivered into a 16-oz. flask, containing a weighed quantity of pure sodium carbonate dissolved in a small quantity of water. 1·10 grms. of sodium carbonate are taken for every 1 grm. of acid. This weight of the nominally dry carbonate is placed in a tared platinum crucible, gently ignited over a spirit flame for ten minutes, cooled in the desiccator with a cover on the crucible, and the exact weight then taken. After the acid has been run into the sodium carbonate solution, the liquid is heated to boiling to expel most of the carbonic acid, then made quite cold, and the excess of sodium carbonate determined by titration with decinormal acid, using methyl orange as indicator. In order that the end point of the titration may be sharply observed, the colour of the liquid should be compared with that of an equal volume of pure water tinted with the same quantity of methyl orange and contained in an exactly similar flask. The following is an example of the calculation :—

		Grms.
Weight of sulphuric acid titrated $= \frac{1}{5} \times 11\cdot1110$	=	2·2222
Weight of dry Na_2CO_3 taken	=	2·4493
N/10 acid, 13·38 c.c. $= Na_2CO_3$ 13·38 × ·0053	=	·0710
Weight of dry Na_2CO_3 neutralized	=	2·3783
Equivalent weight of H_2SO_4	=	2·1980
∴ *Strength of Acid* $= 2\cdot1980 \div 2\cdot2222 \times 100$	=	98·98% H_2SO_4

If the acid be weaker than 97 per cent., it is rejected ; if stronger, it is diluted to exactly 97 per cent. strength by adding to a weighed quantity, say 1 kilo., the requisite quantity of pure water, which may be measured from a delicate burette and well stirred into the acid. The reagent thus prepared is preserved for use in a capped ether bottle ; the stock is kept in the 'Winchester,' the stopper of which, after wiping free from acid, is smeared with a little vaseline and tied down.

Beakers, tall form, 4 inches high by $2\frac{1}{2}$ inches in diameter. These fit into a nest of cotton-wool contained in a 40-oz. lipped beaker.

A 10 *c.c. burette*, with glass tap. The orifice of the jet is reduced by holding it in the Bunsen flame until, with the tap turned full on, 10 c.c. of the sulphuric acid take one minute, within a second or two, to flow out.

A Centigrade thermometer, graduated in single degrees from 0° to 100°.

In making a test, the temperature of the air of the room is first of all ascertained, and the acid is then brought to the same temperature by warming the bottle by the hand or by cooling it in water. Exactly 50 grms. of the oil, having been weighed into the beaker, are stirred with the thermometer and brought to the same temperature as the acid, and the beaker is then placed in the cotton-wool nest. The burette having been filled with the acid and covered with a glass cap, the beaker is brought under it, the tap is opened wide, and 10 c.c. of acid are allowed to run into the oil, all the time stirring the oil and the acid most thoroughly together. After the acid is all in, the stirring is continued until the mercury ceases to rise. The final temperature is read off, the initial temperature is deducted, and the difference is the rise of temperature.

When a number of samples are being tested, a thermometer is kept suspended near the burette to record the temperature of the air, and, if this alters, the initial temperature of the oils must be altered to correspond. Immediately after testing each oil the burette is refilled with acid and capped, and the neck of the bottle is carefully wiped dry and capped. If these directions are followed, very good results may, with practice, be obtained.

This test is most useful in comparing one sample of oil with another, as in controlling the quality of the deliveries of oil purchased to sample. As the results obtained are influenced not only by the strength of the acid used but also by the exact *modus operandi*, each observer must construct a table of results for himself, by testing several pure samples of each oil he requires to examine. Table LXXII. will serve to show, approximately, the results obtained with some well-known oils.

In testing oils which evolve more heat than cottonseed oil, the chemical reaction becomes so violent that the liquid froths out of the beaker ; therefore, the test cannot be made unless the oil is diluted. For this purpose olive oil is suitable ; *e.g.* 20 grms. of linseed oil diluted with 30 grms. of olive oil give a moderate thermal effect. The olive oil must be tested separately to ascertain the rise of temperature obtained with it alone ; the thermal rise of the linseed oil is then calculated as shown by the following example :—

$$\text{Rise of temperature of the mixture, observed,} \qquad 77 \cdot 2°$$

$$\text{Effect due to 30 grms. of olive oil} = \frac{3}{5} \times 42° = \qquad 25 \cdot 2°$$

$$\text{Effect due to 20 grms. of linseed oil,} \qquad 52 \cdot 0°$$

$$\therefore 50 \text{ grms. of linseed oil would rise } \frac{5}{2} \times 52° = \qquad 130°$$

TABLE LXXII.

Name of Oil.	Rise of Temperature with 97% Sulphuric Acid. Degrees Centigrade.
Animal (tallow) oil, . . .	35°–42°
Olive oil, ...	40°–45°
Neatsfoot oil, ...	42°–49°
Arachis oil, ...	49°
Horse oil, ...	46°–55°
Castor oil, ...	56°–66°
Rape oil, ...	58°–64°
Sesamé oil, ...	63°–65°
Ravison oil, ...	75° and over
Cottonseed oil, ...	75°–85°
Poppyseed oil, ...	87°–89°
Nigerseed oil, ...	100°
Seal oil, ...	105°
Menhaden oil, ...	125°
Linseed oil, ...	128°–145°

Specific Temperature Reaction.—Thomson and Ballantyne[1] have proposed to avoid the trouble involved in the preparation of an acid of known strength by a new method of recording results. Instead of stating the rise of temperature in degrees, they express the result in terms of the rise of temperature with water at 20° C., taken as 100.

Exactly 50 c.c. (= 50 grms.) of water are delivered into the beaker from a pipette, brought to 20° C., and mixed with 10 c.c. of sulphuric acid also at 20° C. The acid is run into the water exactly in the same way and at the same rate as into an oil, but the experiment is not so easy, as in stirring the water and acid together in the absence of a lubricant one is very apt to crack the beaker, and the temperature with water does not remain for some time stationary at the maximum, as with oil, but quickly begins to fall. Having, however, successfully made the experiment, preferably in duplicate, the oil is tested in the same way and in the same beaker. The result with oil is then divided by the mean result with water, and the quotient, multiplied by 100, is the ' *Specific Temperature Reaction.*' Table LXXIII., by Thomson and Ballantyne, shows the results they obtained by operating in this way with acids of three different strengths.

Thomson and Ballantyne found, when testing the same sample of olive oil in two different beakers, one 3 inches and the other 4 inches in height, but both 2 inches in diameter, that the temperature rose 2 degs. higher in the taller beaker; the same difference was observed with water; therefore, in whichever beaker the experiments were made, the specific temperature reaction, calculated from the thermal effects with water and oil in the same beaker, were almost identical, the figures being 93·5 and 93·8.

[1] *Jour. Soc. Chem. Ind.*, x. (1891), p. 233.

TABLE LXXIII.

Sample.	H₂SO₄ 95·4 per cent.		H₂SO₄ 96·8 per cent.		H₂SO₄ 99·0 per cent.	
	Rise of Temperature °C.	Specific Temperature Reaction.	Rise of Temperature °C.	Specific Temperature Reaction.	Rise of Temperature °C.	Specific Temperature Reaction.
Water, . . .	38·6	100	41·4	100	46·5	100
Olive oil, . .	36·5	95	39·4	95	44·8	96
	...	...	39·0	94	43·8	94
	34·0	88	38·1	92	44·2	95
Rape oil, . .	49·0	127	...	...	58·0	124
Castor oil, . .	34·0	88	37·0	89	...	...
Linseed oil, . .	104·5	270	...	...	125·2	269

The evolution of heat on mixing oils with sulphuric acid proceeds from a variety of chemical reactions; e.g. saponification or hydrolysis of the glycerides, sulphonation of the fatty acids and glycerol, and, as the temperature rises, destructive oxidation accompanied by charring and evolution of sulphur dioxide. The evolution of heat depends largely upon the proportion and nature of the unsaturated fatty acids present, and bears a more or less definite relation to the iodine value. This relation, however, according to Hehner and Mitchell, is quite different with different oils and fats, unlike the relation between the bromine thermal value and the iodine value, which is nearly the same for most oils and fats. The following comparative results obtained by Archbutt with rape oil, show that although the iodine value may be calculated very nearly from the Maumené figure, the bromine thermal value is a more reliable basis for calculation, notwithstanding

TABLE LXXIV.

Sample of Rape Oil.	Iodine Value by Hubl's Process.	Iodine Value calculated from the Bromine Thermal Value. β × 5·92.	Iodine Value calculated from the Sulphuric Acid Thermal Value. σ × 1·67.
No. 1	102·7	102·7	99·4
„ 2	103·3	103·0	101·4
„ 3	103·1	102·4	101·9
„ 4	105·7	104·8	106·5
„ 5	104·6	105·4	104·3
„ 6	106·2	105·9	106·0
„ 7	108·1	108·0	109·9
„ 8	109·4	110·1	111·4

the fact that the multiplier in the latter case is more than three times as large as in the former.

O.—OXIDATION AND GUMMING OF LUBRICATING OILS.

I. **Fixed Oils.**—No absolute quantitative method of determining the oxidizing properties of lubricating oils is known. The behaviour of the different fixed oils when exposed in thin films to the air at the ordinary or a slightly elevated temperature, leads to their classification in three divisions, viz. :—(1) *drying oils*, which by oxidation soon solidify to a varnish and therefore include the paint oils ; (2) so-called *non-drying oils*,[1] which remain fluid for long periods and comprise the best lubricating oils ; and (3) *semi-drying oils*, which form an intermediate class, drying but slowly, yet too oxidizable to be well adapted for lubricating. Rape oil, however, which is the least oxidizable of the semi-drying oils, is largely used as a lubricant by large consumers, owing to its comparatively low cost.

In the examination of olive oil, lard oil, sperm oil, and other well-known lubricating oils belonging to the non-drying class, also fats such as tallow, it is as a rule sufficient to prove the absence of adulterants belonging to the drying and semi-drying classes by means of the ordinary physical and chemical tests, paying special attention to the iodine value, which is increased by the presence of the more easily oxidizable oils. But with rape oil the case is different. Genuine rape oils differ considerably in gumming properties, and a special oxidation test is not only useful but practicable, as rape oil is sufficiently oxidizable to give a decided result in a reasonable time. The following simple comparative test is usually made :—

(a) **Watch-glass Test.**—1 grm. of the sample of oil is weighed on a watch glass, the same weight of a standard sample is weighed on another watch glass of the same curvature, and the two glasses are placed side by side in a boiling-water oven, where they are left undisturbed for a certain number of hours. A good practice is to place the glasses containing the oils in the oven at, say, 5 p.m., and take them out at 9 a.m., *i.e.* after an interval of sixteen hours. The condition of the oils is then examined when cold.

Tested in this way, and using 1 grm. of the substance, rape oil of the very best quality does not dry, and does not appear to have thickened much when caused to flow by inclining the glass ; inferior samples will have crept up and formed dry spots on the sides of the glass, and most rape oils will have thickened more or less considerably. The result of this test, considered in conjunction with the physical and chemical data, is of considerable assistance in judging the quality of rape oil.

[1] Livache has shown (*Jour. Soc. Chem. Ind.*, xiv. (1895), p. 811) that all fixed oils, whether vegetable or animal, and even fats, if exposed to the air at sufficiently high temperature (120°–160° C.), sooner or later dry up, forming solid elastic product similar to that obtained from the drying oils.

The same test is sometimes useful in the examination of olive oil. In this case 0·5 grm. should be used for the test, the other conditions remaining the same. Good olive oil will change very little in sixteen hours ; inferior oil, dark green or greenish brown in colour, will thicken considerably.

The object of using a weighed quantity of oil is merely to ensure uniform conditions, equal weights of oil in glasses of the same curvature exposing the same surface area ; it is not worth while to attempt to get more out of the test by weighing the oil after exposure, as the changes in weight due to oxidation are small and erratic, some of the products of oxidation being volatile at 100° C.; they are also affected by variable traces of moisture in the oils, and no satisfactory result is thus obtained. (See Livache's test.)

(*b*) **Film Test.**----A less simple, but for some purposes a better test than the above, is made by exposing the oil in a film on a glass plate at a temperature of 50° C. It is not easy to obtain continuous films, nor films of uniform thickness, and unless they are uniform the results are not comparable. The least trace of moisture on the surface of the glass, even the film of moist air condensed on all apparently dry cold surfaces, causes some oils to draw up into irregular patches and drops. This may be avoided by first heating the glass strongly and painting it with the oil while still hot.

Pieces of plate glass, say 3 inches square and $\frac{3}{16}$ inch thick, are carefully cleaned, wiped dry, and weighed. Each glass is numbered, and its approximate weight is marked on a card. The glasses are first heated in an air-oven to 200° C. for about half to one hour, then taken out and laid upon pieces of cork. As soon as they have cooled down to about 100°, the upper surface of each is thinly painted over, by means of a clean camel-hair brush, with the oil to be tested, and the glasses are then left to become quite cold. When cold they are placed again on the balance, and more oil is dropped upon the centre of each plate until exactly 0·1 grm. has been made up. The plates are then laid, with the oiled sides upwards, upon a levelled sheet of plate glass, in an oven furnished with a regulator by which the temperature can be maintained at the temperature of 50° C. The oil last added will gradually spread over the surface of the glass. At intervals of a few hours the plates are removed from the oven, allowed to cool down to the temperature of the laboratory, and the condition of the oil tested by touching with the finger.

Even with the precautions above stated, the film will be thicker in some parts than others, and will not always dry at a uniform rate ; but, by making duplicate tests, very fairly comparable results may be obtained. As a result of several tests made in this way it has been found that refined cottonseed oil dries to a varnish in from eighteen to twenty-four hours, refined rape oil requires about forty-eight hours to dry to the same extent, whilst olive oil does not dry up in thirteen days.

The following results by Holde[1] were obtained by spreading '1

     [1] *Die Untersuchung der Schmiermittel*, p. 98.

drop' of the oil on a glass plate measuring 5 × 10 centimetres and exposing to air at 50° C. for twenty-four hours. The film thus obtained would be thinner than that formed in the above-described test, and might be expected to dry more quickly.

TABLE LXXV.—EFFECT OF EXPOSING SOME FIXED OILS IN THIN FILMS TO AIR AT 50° C. (*Holde*).

Kind of Oil.	Consistence after 24 Hours' Exposure.	Kind of Oil.	Consistence after 24 Hours' Exposure.
Sperm oil, . .	Unchanged.	Mustard oil, .	Sticky, to dry.
Castor oil, . .	,,	Earthnut oil, .	,,
Bone oil, . .	,,	Sesamé oil, , .	Dry.
Olive oil, . .	Unchanged, or slightly thickened.	Cottonseed oil, .	,,
		Sunflower oil, .	,,
Almond oil, . .	Perceptibly thickened.	Poppy oil, .	,,
Crude rape oil, .	Perceptibly thickened, to sticky.	Fish oil, . .	,,
		Cod-liver oil, .	,,
Refined rape oil, .	Sticky, to dry.	Train oil, . .	,,
Whale oil, . .	Thicker, to sticky.		

(*c*) **Livache's Test. Increase of Weight by Oxidation.**—Any attempt to measure the rate of oxidation of fixed oils by ascertaining the increase of weight at elevated temperatures is met by the difficulty that some of the products of oxidation are volatile. Thus Kissling[1] found, by passing air through linseed oil heated to 100° C., that, of 0·87 per cent. of oxygen taken up daily, 0·46 per cent. was carried away in the form of volatile acids of the methane series, carbon dioxide, and other products. Experiments by the same author on oils exposed to the air at 100°–105° C. in clock glasses showed that the loss of weight by volatilization frequently exceeded the gain of weight by oxidation. On the other hand, the gain of weight at the ordinary temperature is much too slow to be made the basis of a practical test.

Livache, however, has shown that the rate of oxidation is greatly accelerated by mixing the oil with finely-divided copper, tin, or lead, the latter giving the best results.

The lead is prepared from solution of a lead salt by precipitation with sheet zinc, washing the precipitate well with water, alcohol, and ether, and drying in vacuo. About 1 grm. of the dry powder is spread out on a large tared watch-glass, and an accurately weighed quantity, somewhat over 0·5 grm. but not exceeding 0·7 grm., of the oil is spotted over it from a pipette, taking care that the drops do not run into one another. The whole is then weighed and allowed to remain exposed to light and air at the ordinary temperature.

Drying oils tested in this manner commence to gain weight rapidly, the maximum increase taking place in a few days, whilst the non-drying oils must be left for fully seven days before any useful result

[1] *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 479.

is obtained. Evidently, this test is unsuited for the systematic examination of lubricating oils, though it may be found useful in special cases.

Livache obtained the following results :—

TABLE LXXVI.—INCREASE OF WEIGHT OF OILS BY OXIDATION.

Kind of Oil.	Percentage Increase of Weight.		
	Of Oil after		Of Fatty Acids after 5 Months.
	Two Days.	Seven Days.	
Linseed oil, ...	14·3	...	11·0
Walnut oil, ...	7·9	...	6·0
Poppyseed oil, . . .	6·8	...	3·7
Cottonseed oil, . . .	5·9	...	0·8
Beech nut oil, . . .	4·3	...	2·6
Colza oil, ...	nil.	2·9	2·6
Rape oil, ...	,,	2·9	0·9
Sesamé oil, ...	,,	2·4	2·0
Arachis oil, . . .	,,	1·8	1·3
Olive oil, ...	,,	1·7	0·7

(*d*) **Bishop's Test.**[1]—Bishop has modified Livache's test by dissolving manganese resinate in the oil to be tested and using an inert absorbent, viz. ignited silica, instead of spongy lead.

Purified manganese resinate is prepared by digesting the commercial article in ether, filtering, distilling off the solvent, and powdering the dry residue. Two per cent. by weight of this is added to 5-10 grms. of the oil previously weighed in a beaker, and the mixture is heated on the water-oven, with occasional agitation, until the resinate is dissolved (taking five to ten minutes); it is then allowed to cool.

1 grm. of freshly ignited precipitated silica is next weighed in a flat-bottomed capsule of 5·5 cm. diameter, containing a small glass rod, and as nearly as possible 1·02 grm. of the mixture (1 grm. oil + 0·02 grm. resinate) is distributed from a fine pipette in small drops all over the surface. The whole is then weighed. The oil and silica are intimately mixed by means of the glass rod, the mixture is spread out in a layer of uniform thickness all over the bottom of the dish, then exposed to air at 20° to 30° C., and weighed at intervals of six hours. After each weighing, the contents of the dish are stirred afresh.

In this test, oxidation takes place most rapidly within a limited range of temperature, which is not necessarily the same for each oil. Thus, between 17° and 28° C. linseed oil reached the maximum weight in from twenty-four to thirty hours from the commencement ;

[1] *Monit. Scient.*, 1896, 259.

ifter that there was a gradual loss of weight. Hempseed, poppyseed, walnut and cottonseed oils reached the maxima in from twenty-four to twenty-eight hours at 22°–28° C., whilst sesamé oil at the same temperature took from seventy-two to ninety-six hours. Arachis oil increased 6·7 per cent. in weight in ninety-six hours at 14°–34·5° C.; another sample gained only 4·8 per cent. in 144 hours at 17°–23° C. Colza and olive oils gain weight very slowly; although a change is perceptible within twenty-four hours, the maximum is not reached for many days or even weeks. Experiments, however, showed that the adulteration of olive oil with oils of more strongly marked drying character caused the most marked effect in the first twenty-four hours. See Tables LXXVII. and LXXVIII.

TABLE LXXVII.—CHANGE OF WEIGHT (PER CENT.) BY OXIDATION
OF COLZA OIL (*Bishop*).

Number of Hours Exposed.	Colza Oil (French). Sp. Gr. 0 9142 at 15° C.		Colza Oil (Indian). Sp. Gr 0 9137 at 15° C.	
	Temp. 28° 20°.	Temp. 20°–15°.	Temp. 28 –20°.	Temp. 20°–15°.
6	− 0·20	− 0·10	− 0·20	− 0·10
22	+2·25	+0·30	+1·10	± 0·0
24	3·20	0·50	1·90	+0·20
30	4·00	1·80	2·90	0·90
48	4·90	4·20	3·80	3·40
72	5·50	...	4·50	...
96	5·80	5·60	5·00	4·70
192	...	5·80	...	5·10
288	6·40	...	5·80	...
432	...	6·40	...	5·90

This test deserves further investigation in connection with lubricating oils.

(*) **Oxygen Absorption Test.**—Angus Smith[1] in 1870 used the following test in examining some samples of rape oil intended for lubricating :—A measured quantity of the oil, from 3–5 c.c., was confined over mercury in a graduated tube filled with oxygen. Absorption took place slowly but steadily during twenty-two days, when the experiment was stopped and the total volume of gas read off.

						Ratio.
100 c.c. of oil	No. 1	absorbed	37·8 c.c.			148
„ „	No. 2	„	47·8 c.c.			187
„ „	No. 3	„	25·5 c.c.			100

[1] Private report.

TABLE LXXVIII.—CHANGE OF WEIGHT (PER CENT.) BY OXIDATION OF PURE AND MIXED OLIVE OIL (*Bishop*).

Number of Hours Exposed.	Olive Oil. Sp. Gr. 0·9155 at 15° C.		
	Pure.	+20% Arachis Oil.	+20% Cottonseed Oil.
	Temp. 14°-34·5°.	Temp. 14°-34·5°.	Temp. 14′-34·5°.
24	+0·80	+1·75	+3·25
48	2·40	3·00	4·25
72	3·40	4·00	4·80
144	4·70	4·75	5·60
384	5·30	5·55	6·05
	Temp. 17′-23°.	Temp. 17′-23°.	Temp. 17′-23°.
24	− 0·30	− 0·30	− 0·30
48	− 0·20	− 0·20	+0·50
72	+0·90	+1·70	2·90
144	2·20	3·10	3·80
264	2·30	3·50	3·90

A summary of Bishop's results is given in the following table :—

TABLE LXXIX.

Description of Oil.	Specific Gravity.	Increase of Weight Per Cent.	Mean Values.
Linseed oil (French), . .	0·9327	17·70–16·40	17·05
„ (La Plata), . .	0·9304	15·45–15·00	15·20
Hempseed oil, . . .	0·9287	14·55–14·30	14·40
Poppyseed oil (French), . .	0·924	14·50–13·90	14·20
Walnut oil, . . .	...	13·7?	13·70
Cottonseed oil, . . .	0·924	8·60	8·60
„ (chilled), .	0·923	9·60 9·30	9·45
Sesamé oil (Senegal), .	0·9215	8·95– 8·50	8·70
„ (Indian), .	0·921	7·40	7·40
Arachis oil (African), . .	0·916	6·70	6·70
„ (white), . .	0·916	6·50	6·50
Colza oil (French), . .	0·9142	6·40 ?	6·40 ?
„ (Indian), . .	0·9137	5·90– 5·80 ?	5·85 ?
Olive oil, ...	0·9155	5·30 ?	5·30 ?

The volumes of oxygen absorbed in the first forty-eight hours were approximately in the same ratio. Angus Smith considered that the lubricating value of these samples would be in the inverse order of their oxygen-absorbing power.

Fox [1] has described the following method : About 1 grm. of the oil is sealed up with 0·5 grm. of precipitated lead in a glass tube having a capacity of about 100 c.c. The whole is then heated in an oil-bath for several hours at 105° C., when the amount of oxygen absorbed is determined by noting the decrease in volume of gas in the tube. The following results were thus obtained :—

Kind of Oil.	c.c. of oxygen absorbed by 1 grm. of oil.
Linseed oil, ...	126 to 191
Cottonseed oil, ...	24·6
Rape oil (brown), ...	20·0
Colza oil, ...	17·6
Olive oil, ...	8·2–8·7

Bach,[2] following Fresenius, used a similar method, omitting the lead. A known quantity of oil was heated for ten hours with oxygen in a sealed tube of 100–125 c.c. capacity in an air-bath at 110° C. The point of the tube was then broken under water and the absorbed oxygen calculated from the volume of water drawn in. The results given in Table LXXX. were thus obtained.

TABLE LXXX.

Kind of Oil.	c.c. of oxygen absorbed by 1 grm. of oil.
Rape oil, ...	166
Olive oil, ...	144
Cottonseed oil, ...	111
Rosin oil, ...	181
Rosin oil, redistilled, so-called 'cod oil' (Lewkowitsch), ...	96·3
Mineral lubricating oil (·865), . . .	4·8
,, ,, (·877), . . .	·7
Russian mineral oil, ...	·74
Cylinder and valve oils, . . .	·10–·45

Holde [3] describes the following method. From 1–1·5 grm. of freshly-ignited pumice stone, in grains about the size of mustard-seed, is placed in a glass tube 30–40 cm. long and 20–30 mm. in diameter, sealed at one end, and from 0·3–0·5 grm. of the oil is slowly dropped on to the pumice from a tared beaker ; the exact weight added is ascertained by weighing the beaker afterwards. The open end of the

[1] Analyst, viii. (1883), p. 116.
[2] Jour. Soc. Chem Ind., viii. (1889), p. 990.
[3] Die Untersuchung der Schmiermittel, pp. 96 and 100.

:ube having been drawn out and allowed to become cold, the air is lisplaced by oxygen and the tube is quickly sealed with a fine blow->ipe flame. After heating in a water-bath for several hours, the end >f the tube is broken ·off under water, and the volume of oxygen ibsorbed is measured. The most suitable temperature and time of 1eating depend upon the kind of oil experimented upon. Three 1ours' heating in a boiling-water bath were given in the experiments the results of which are recorded in the following table :—

TABLE LXXXI.

Description of Oil.	c.c. of oxygen, reduced to 20° C., and 760 mm., absorbed by 1 grm. of oil.	
	Single Values.	Mean Values.
Cottonseed oil, ...	68·7	68·7
Brown rape oil, . . .	45·5 ; 49·7	47·6
Olive oil, ...	33·3 ; 34·0	33·7
Mixture of bone oil and refined rape oil, ...	32·1 ; 28·1 ; 33·0 ; 28·0	30·3
Mixture of bone oil and refined rape oil, . . . `. .	(29·9) ; 24·7 ; 22·0 ; 22·2	23·0
Sperm oil, ...	24·5 ; 23·9 ; 25·3 ; 24·4	24·5
Sperm oil, ...	18·3 ; 16·6 ; 14·2	16·4

II. **Mineral Oils.**—Although, as is shown by Bach's experiments,[1] nineral lubricating oils are able to absorb small quantities of oxygen vhen heated with it, the amount of oxidation which occurs under irdinary conditions with good mineral oils is practically nil. The hickening or 'gumming' of such oils, when it does occur, is due :hiefly to the evaporation of the more volatile hydrocarbons and the oncentration of asphaltic, resinous, or tarry matters in the residue. Jumming is most marked in the case of the dark residuum-containing ils used for railway and rough work ; the refined, pale and charcoal-iltered oils, from which the resinous and asphaltic constituents have >een removed, undergo scarcely any change except a thickening due o evaporation when heated. Useful information may, nevertheless, >e obtained, when comparing one mineral oil with another, by heat-ng 1 grm. in a shallow dish in a water-oven for several days. Some nineral oils deposit carbon and become thick and sticky when thus ested.

The results of experiments by Holde,[2] who has paid considerable attention to this subject, are contained in Tables LXXXII. (A), .XXXIII. (B), and LXXXIV. (C), which show the behaviour of some

[1] See also Ostrejko, *Jour. Soc.-Chem. Ind.*, xv. (1896), pp. 26, 345, and 645.
[2] *Die Untersuchung der Schmiermittel*, pp. 88-99.

mineral lubricating oils tested by him when exposed to the air in thin and thick layers at temperatures of 50° and 100° C.

In Table A (p. 274) the behaviour of pale refined oils is compared with that of dark 'reduced' oils, and the greater tendency of the latter to thicken and form sticky or 'gummy' residues will be observed.

The results in Table B (p. 278) are intended to show the behaviour of very asphaltic Hünigsen petroleum in its crude state and also after the extraction of part of the tarry matter by petroleum spirit and alcohol-ether.

In Table C (p. 276) quantitative results are given, showing the amount of evaporation resulting from the exposure of mineral oils to 100° C. for several months in thicker layers (0·21–0·24 grm. of oil with a surface of about 75 sq. cm.). The pale, very fluid, and non-resinous 'paraffin oil,' No. 5, from the lowest lubricating oil fractions, gradually evaporated in the course of fifteen months, without leaving a trace of resin behind; the more viscous, brownish-yellow 'motor' oil left a small solid residue, consisting partly of resin originally contained in the oil and partly (as the dark colour of the residue and its insolubility in petroleum spirit proved) of oxidized hydrocarbons formed during the heating. The very viscous oil No. 7, consisting of a distillate of very high boiling-point, evaporated and dried very little; the same oil, partly deresinified by treatment with alcohol, dried still less. The oils which dried most were the residuum-containing oils Nos. 1 to 4, of which again those purified with alcohol-ether dried less than the untreated oils. The Russian oil No. 1 contained, as the viscosity shows, lower boiling hydrocarbons than No. 7, and therefore, although it resinified more quickly than the latter oil, the residue was essentially more fluid. All the resinous residues left by heating mineral oils are incompletely soluble in petroleum ether, even though the original unheated oils (as Nos. 6–8) may have been completely soluble; these residues are, however, easily soluble in benzene.

Holde summarizes the results of his experiments as follows:—
When exposed to the air in thin films (1 drop of oil on a 5 × 10 cm glass plate) the pale and dark-coloured distilled mineral oils do no resinify after several months' exposure, either at the ordinary temperature or when heated to 50° or 100° C. Dark residuum containing oils by long exposure at ordinary temperatures resinify very little, but at 50°–100° C. a marked thickening, and, with very tarry oils, even complete resinification, occurs, whilst the greater proportion of the fluid hydrocarbons evaporate, and the remainder oxidize adding to the tarry and asphaltic contents of the residue.

In thicker layers (0·20–0·25 grm., exposing a surface area of 7. sq. cm.), the pale-coloured, non-resinous distillates do not resinify even at 100° C., but the dark-coloured distillates, containing 1–3 per cent. of resin, leave partly resinous residues. Dark residuum containing oils, similarly treated, yield sticky or solid products, even after the first few months, and after fifteen months the residues are quite hard and pitchy.

18

TABLE LXXXII. (A).—CHANGES UNDERGONE BY MINERAL

('1 drop' of Oil spread

No.	Description.	Colour.	Relative Efflux Time at 20° C. (*Engler*). Water=1; Refined Rape oil=12·2.	Specific Gravity at 20° C.	Flashing-point ° C. P=Pensky Closed Cup. O=Open Cup.
	PALE OILS; TRANSPARENT IN 15 MM. TUBE.				
1	So-called 'paraffin oil,' . .	Colourless	5·9	0·866	158° P
2	American 'motor' oil, .	Reddish brown, fluorescent	11·3	.	..
3	Russian heavy machine oil, .	Reddish-brown	27·6	0·904	138° P
4	Heavy machine oil, .	Light coloured	66·4 at 15° C.	0·899	206° P
5	,, . . .	,,	38·9	0·903	190° P
6	,, . . .	,,	35·0	0·903	195° P
7	,, . . .	,,	42·0	0·905	187° P
8	Russian heavy machine oil, .	Reddish-brown	6·2 at 50° C.	0·904	186° P
	DARK OILS; OPAQUE IN 6 MM. TUBE.				
9	Russian axle oil, . .	..	45·5	0·906	176° O
10	Axle oil, ...	..	46·0	0·906	173° O
11	,, . . .	..	37·0	0·907	164° O
12	,, . . .	..	37·6	0·908	170° O
13	Lubricating oil, . .	..	30·6	0·935	163° P

LUBRICATING OILS WHEN HEATED IN THIN LAYERS (*Holde*).

on a 5 × 10 cm. Glass Plate.)

Condition of Oil Film after heating to							
50° C.				100° C.			
90 Hours.	140 Hours.	190 Hours.	300 Hours.	35 Hours.	70 Hours.	120 Hours.	300 Hours.
almost completely evaporated; residue oily.	as before.	mere trace of oily residue.	..	all but traces evaporated.	completely evaporated.	..	..
very much evaporated, perceptibly thickened.	all but traces evaporated; residue only.	as before.	..	greater part evaporated; residue oily.	as before.	mere trace of oily residue.	..
unchanged.	unchanged.	much evaporated; residue oily.	as before.	greater part evaporated; residue only.	all but trace of oily residue evaporated.	..	..
much evaporated, otherwise unchanged.	greater part evaporated; residue oily.	as before.	as before.	greater part evaporated; residue oily.	as before.	all but oily traces evaporated.	..
unchanged.	much evaporated; residue oily.	as before.	the greater part evaporated; residue oily.	..	..	..	..
unchanged	much evaporated; residue oily.	as before.	the greater part evaporated; residue oily.	..	greater part evaporated; residue oily.	..	..
unchanged.	..	partly evaporated; residue oily.	the greater part evaporated; residue oily.	..	..	..	..
much evaporated, but residue oily and unchanged.	the greater part evaporated; residue oily.	all but traces evaporated; residue oily.	..	greater part evaporated; residue oily.	all but traces of oily residue evaporated.	..	..
very much thicker.	much thicker	largely evaporated, much thicker.	much evaporated, very thick.	barely fluid, very slightly sticky.	as before.	still less fluid.	**sticky.**
very much thickened to very slightly sticky.	much thicker, slightly sticky.	much thicker, slightly sticky.	mostly evaporated; otherwise as before.	..	..	..	..
very much thickened.	as before.	as before.	much evaporated; oily.	almost dry; oily when warm.	..	..	..
very much thickened.	much evaporated, considerably thickened.	as before.	mostly evaporated; residue oily.	barely fluid to slightly sticky.	as before.	as before.	very much evaporated, otherwise as before.
very much thickened.	a little thicker	much evaporated; a little thicker.	much evaporated; thick to sticky.	sticky, barely fluid.	barely fluid, very slightly sticky.	as before.	(175 hours) much evaporated, and almost solid even when warm.

TABLE LXXXIV. (C).—RESINIFICATION OF MINERAL

Number.		1.	2.	3.
Description.		Russian, brown-black, opaque, railway axle oil.	No. 1, deresinified with alcohol-ether (4 : 3); clearer.	Oelheimer, brown-black, opaque, axle oil.
Relative efflux time at 20° C. (Engler). Water=1.		45·5	..	29·6 at 40°
Flashing-point.		176° C. (open)	..	161° C. (*Pensky*)
Weight taken (grm.).		0·2109	0·2103	0·2252

	Months.	Total Loss of Weight (grm.).	Consistence and Appearance.	Total Loss of Weight (grm.).	Consistence and Appearance.	Total Loss of Weight (grm.).	Consistence and Appearance.
	⅓	0·0429	fluid	0·0444	fluid	0·0304	viscous
	½	0·0541	viscid, to slightly sticky	0·0528	fluid	0·0354	part greasy, part solid
	1	0·0636	viscid, to slightly sticky	0·0619	decidedly viscous	0·0379	part greasy, part solid
Area of exposed surface about /5 sq. cm. Time of heating, 7-8 hours at 100° C. every day except Sundays.	2	0·0690	..	0·0734	viscous	0·0428	almost all solid
	3½	0·0749	very viscous; decidedly sticky	0·0808	..	0·0436	almost all solid
	5	0·0787	..	0·0808	part sticky, part greasy	0·0444	almost all solid
	9½	0·0773	greater part waxy, rest greasy	0·0876	part sticky, part greasy	0·0470	entirely solid and resinous
	15	0·0725	soft wax	0·0832	thick jelly	0·0334	entirely solid and resinous

OILS IN THICK LAYERS AT 100° C. (*Holde*).

4.	5.	6.	7.	8.
No. 3, deresinified by alcohol-ether (4 : 3).	Russian, colourless, clear, transparent, 'paraffin oil.'	American brown-yellow, fluorescent, motor oil.	Russian red-brown distillate, made in laboratory.	No. 7, deresinified by 70 per cent. alcohol.
..	5·9	11·6	105·9	..
	158 C. (*Pensky*)	103° C. (*Pensky*)	..	..
0·2208	0·2042	0·2430	0·2170	0·2148

Total Loss of Weight (grm.).	Consistence and Appearance.	Total Loss of Weight (grm).	Consistence and Appearance.	Total Loss of Weight (grm.).	Consistence and Appearance.	Total Loss of Weight (grm.).	Consistence and Appearance.	Total Loss of Weight (grm.).	Consistence and Appearance.
0·0080	viscid	0·0988	oily, fluid	0·0124	oily	..	oily	..	oily
0·0096	partly sticky	0·1170	oily	0·0262	..	..	.	..	..
0·0121	partly sticky	0·1302		0·0458	..	0·0024	oily	0·0026	..
0·0130	partly sticky	0·1522	oily	0·0774	..	0·0109	..	0·0078	..
0·0150	partly a thick jelly	0·1622	.	0·0952	.	0·0173	oily	0·0108	..
0·0148	..	0·1727	oily, darkened in colour	0·1114	oily	..	..		..
0·0148	greater part solid, the rest greasy	0·1846	traces of oily residue	0·1304	greater part waxy, rest greasy	0·0315	viscous oil	0·0204	thick oily, partly solid
0·0050	all solid and resinous, but softer than 3	0·1876	traces of oily residue	0·1533	solid, brown	0·0330	thick jelly, but part solid	0·0272	viscous, partly solid

TABLE LXXXIII (B).—BEHAVIOUR OF CRUDE HÄNIGSEN (HANOVERIAN
PETROLEUM HEATED TO 50° C. (*Holde*).

('1 drop' of Oil-spread on a 5 × 10 c.m. Glass Plate.)

Previous Treatment.	Consistency at	Number of Hours heated to 50° C.			
		21	42	70	300
None	ordinary temperature	very sticky	sticky, solid	..	..
	40°-50°	oily	very sticky	..	.
Partly freed from asphalt by petroleum spirit ('benzine')	ordinary temperature	very sticky	very sticky	sticky, solid	..
	40°-50°	oily	sticky, scarcely oily	sticky, solid	..
Purified from asphalt by benzine, and from pitch by ether-alcohol	ordinary temperature	moderately sticky	sticky	solid and sticky	solid and sticky
	40°-50°	oily	viscid	viscid	viscid

P.—SPONTANEOUS IGNITION OF OILY MATERIALS.

It is well known that oily rags, oily cotton waste, and similar materials are liable to heat and take fire spontaneously, and that numerous fires have originated in this way; a brief discussion of this subject is, therefore, of importance to all users of lubricants.

The oxidation of oils is a process in which heat is always evolved, but, under ordinary circumstances, the temperature of the oil is not sensibly raised, because the heat, which is evolved slowly, is conducted away as fast as it is liberated. When the rapidity of oxidation is increased by blowing air through a large mass of oil, as in the manufacture of thickened oils, the temperature rises considerably. Conditions most favourable for the generation of heat by oxidation present themselves when a fibrous substance like cotton is saturated with oil and thrown together in a heap, especially in a warm place. Under these conditions the oil, spread out in thin films on the cotton fibres, presents a large surface for oxidation, and the heat being prevented from escaping, owing, chiefly, to the absence of convection currents, raises the temperature of the mass and thereby promotes more vigorous oxidation, which leads to a further and more rapid development of heat, until finally the temperature of ignition of the mass may be reached and it bursts into flame.

The subject has been experimentally investigated by Gellatly, Coleman, Young, and many others, by saturating balls of waste fibre with various oils, placing them in a chamber heated to 212° F. or some lower temperature, and noting the time taken by the mass to inflame. The results obtained have shown that the drying oils, such as linseed, and especially boiled linseed oil, cause ignition most readily, and the non-drying oils least readily, but all drying and semi-drying oils, and even such non-drying oils as olive and lard oil, are capable of causing ignition sooner or later under the conditions named. Mackey has shown by experiments with olive and cotton-seed oils[1] that free fatty acids prepared from these oils are more liable to develop heat and eventually to fire when spread on cotton than the neutral oils themselves,[2] a fact which he considers of importance in relation to fire risks in woollen mills, as recovered cloth-oils and distilled oleines consist largely of free fatty acids. In the experiments recorded in Table LXXXV. (p. 282) it will be noticed, however, that commercial "oleine" and "97 per cent. oleine" heated no more than neutral olive oil.[3] According to Kissling,[4] the generation of heat is influenced to a considerable extent by the nature of the fibrous material, being most rapid with silk, and less, in order, with animal wool, cotton wool, jute, and hemp.

In practice, the risk of fire arising from spontaneous ignition of oily material is greater the more readily oxidizable the oil, and therefore, generally, the higher the iodine value of the oil and the greater the evolution of heat in Maumené's thermal test. Mineral oils, which are practically incapable of oxidation, do not heat at all, and not only are they, therefore, free from the danger of spontaneous ignition, but when mixed with fatty oils in sufficient proportion, which varies according to the nature of the fatty oil, they prevent the risk of fire arising from the spontaneous ignition of the mixture. Given a sufficiently high flashing-point, not below 340°-350° F. (171°-177° C.), the more mineral oil there is in a mixed lubricant the safer the oil as regards the liability to cause a fire; nevertheless, the fire insurance companies consider the fire-risk in textile and woollen mills greater the higher the percentage of 'unsaponifiable matter'[5] in the oil used. This is chiefly owing to the fact that when a fire has once broken out, mineral oils, which, as a rule, flash at a lower tem-

[1] *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 1164.
[2] The difference has to do with the chemical action of the fatty acids on the cotton, as it was not observed when an inorganic material like slag wool was substituted for the cotton.
[3] Compare Richardson and Jaffé, *Jour. Soc. Chem. Ind.*, 1905, p. 534.
[4] *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 479.
[5] Both Mackey and Lewkowitsch have pointed out the fallacy of assuming the 'unsaponifiable matter' to consist, necessarily, of mineral oil, since in recovered wool grease, for example, it may be composed entirely of cholesterols, and should therefore be examined as described in Chap. VII., p. 228. In distilled wool grease, however, hydrocarbons occur, which, though not 'mineral oil,' are undistinguishable from it, and, as regards fire-risk, may be regarded as identical.

perature than the vegetable oils, are more likely to assist in spreading the fire in proportion to the difference of flashing-point (*Mackey*).

Both in the United States and in this country apparatus has been devised specially for the purpose of determining the relative liability of oils to cause spontaneous combustion.

Allbright and Clark's Apparatus,[1] generally known as Ordway's, consists of a double chamber, formed by two tubes placed one inside the other. The outer tube is of wrought iron, 6 inches in diameter, and is closed at each end by discs of wood. The inner tube is of sheet iron, 4 inches in diameter, and 6 inches shorter than the outer tube, and is fitted with overlapping metal covers at each end, which support it centrally within the outer tube, leaving an annular air-space of 1 inch between the two tubes and a space of 3 inches at each end. The apparatus, suitably supported, is heated by a Bunsen burner, and three thermometers, which are inserted into the inner tube through the outer, allow the temperature to be read off.

50 grms. of the oil to be tested are distributed as evenly as possible over 50 grms. of cotton waste, which is then carefully pushed into one end of the inner tube, and a second similar ball of un-oiled waste is inserted into the other end. One thermometer is placed with its bulb in the ball of oiled waste, one in the ball of un-oiled waste, and the third midway between the two. The outer tube is then heated so that the thermometer in the un-oiled waste indicates 100°-101° C., not higher, the maintenance of this temperature being controlled by means of the middle thermometer, which should be kept at about 125° C. Spontaneous heating of the oiled waste is indicated by the temperature of the mass rising above that of the un-oiled waste, and the difference of temperature will be greater and the rise more rapid the more dangerous the oil.

Richards states that this apparatus has been of the greatest use in determining the cause of fires and in estimating the relative safety of oils for use in textile mills. Among other results it has been found that the proportions of neatsfoot and best lard oils which can safely be mixed with mineral oil amounts to from 50 to 60 per cent., whilst not more than 25 per cent. of cottonseed oil can be safely added. That is to say, cotton waste oiled with a mixture of 50 per cent. lard oil and 50 per cent. mineral oil would not be liable to ignite spontaneously, but if the lard oil were adulterated with cottonseed oil, ignition might occur. In either case, a good deal would depend upon the size of the heap of waste and the temperature of the surrounding air.

Mackey's 'Cloth-Oil Tester' (fig. 73)[2] consists of a cylindrical copper water-bath tinned on the inside, measuring externally 8 inches high × 6 inches in diameter, and internally 7 inches high × 4 inches in diameter, provided with a lid having a short central tube D for a thermometer and two longer tubes A and B for promoting the circulation of air. A cylinder of 24-mesh wire gauze C, 6 inches long × 1½ inches in diameter, contains the oiled wool.

14 grms. of the oil to be tested are weighed into a shallow dish containing 7 grms. of pure cotton wool, and after thoroughly incorporating the oil by

[1] Richards, *Jour. Soc. Chem. Ind.*, xi. (1892), p. 547.

[2] *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 940 ; and xv. (1896), p. 90.

hand with the well teased wool, which cannot be too carefully done, as the success of the experiment greatly depends upon the even distribution of the oil, the thermometer is held upright in the middle of the ganze cylinder and the oiled wool is carefully and uniformly packed around it.   Having raised the water in the outer jacket to active ebullition, the cylinder and thermometer are placed in the inner chamber, the lid is carefully slipped down over the thermometer stem, and the latter is fixed in position by tightening up the screw-clamp D.   The position of the thermometer should be such that the red mark on the stem is just visible above D.   The water in the jacket is kept steadily boiling, care being taken that steam is neither drawn down the tube B nor warms the tube A, and the temperature of the wool is read off at intervals.
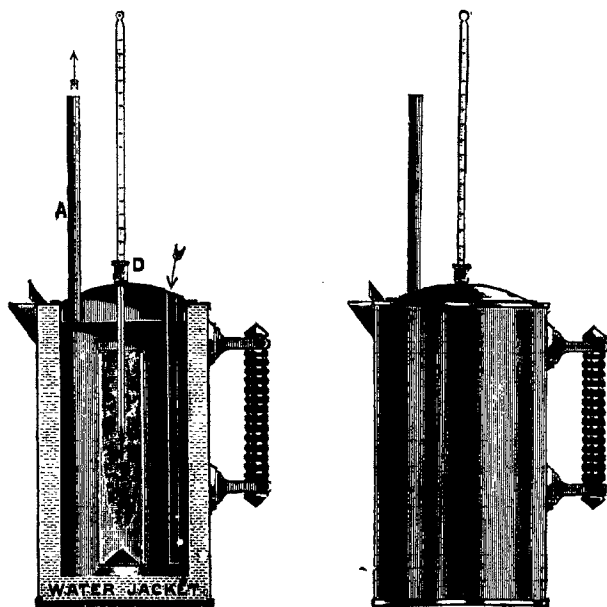
FIG. 73.—Cloth-oil Tester.

It usually takes about one hour for the oiled wool to reach the temperature of the bath (100° C. = 212° F.), and safe oils, like pure olive oil, will not rise much higher; but dangerous oils will continue to heat, and very dangerous oils, such as cottonseed, will rise to 200° C. (392° F.) within one hour and a half.   Generally, the temperature after a certain point is reached commences to rise very rapidly, and when this is the case the thermometer must be withdrawn after reaching, say, 250° C., otherwise it may be damaged.   Mackey states that any oil which, when tested in this way, reaches 200° C. in two

hours, may be regarded as too dangerous for use in mills. The worst class of oil, from a fire insurance point of view, will heat more rapidly than this.

Everyone using the apparatus for the first time should experiment with pure olive and cottonseed oils, comparing his results with those in the following table by Mackey, until he has found how to prepare and pack the mixture of wool and oil so as to obtain similar results :—

TABLE LXXXV.

No.	Oil used.	Temperature in				Maximum.		
		1 hr.	1 hr. 15 m.	1 hr. 30 m.	2 hrs.		H.	M.
		°C. = °F.	°C. °F.	°C. = °F	°C. °F.	°C. = °F.		
1	Cottonseed, . . .	125 = 257	242 - 468	..	.	242 - 468	1	15
2	,, . . .	121 - 250	242 = 468	282 = 540	..	284 = 543	1	35
3	,, . . .	128 = 262	212 414	225 - 437		225 = 437	1	30
4	,, . . .	124 = 255	210 = 410	.		248 - 478	1	35
5	,, . . .	116 = 241	192 = 378	200 = 392	..	200 = 392	1	30
6	,, . . .	118 - 244	191 = 376	202 = 396	..	202 = 396	1	30
7	,, . . .	117 = 243	190 = 374	194 = 381	..	194 = 381	1	30
8	,, . . .	112 = 234	177 351	204 = 399		211 = 412	1	45
9	Olive fatty acids, . .	114 237	177 = 351	..	..	196 = 385	1	25
10	,, ,, .	105 = 221	165 = 329	..		293 559	1	55
11	,, ,, . .	102 = 216	135 - 275	208 = 406	..	226 = 439	1	45
12	White Australian oleine, .	103 = 217	115 = 239	191 = 376	..	230 = 446	1	45
13	Olive (containing 1 °/ free fatty acids),	98 = 208	102 = 216	104 = 219	..	241 = 466	3	25
14	Oleine, . . .	98 = 208	101 = 214	102 = 216	..	110 230	2	8
15	97% oleine, . .	98 - 208	100 = 212	102 - 216	..	172 = 342	3	15
16	Belgian oleine, . .	98 = 208	99 = 210	100 212	..	173 = 343	3	16
17	Olive (neutral), . .	98 = 208	100 = 212	101 = 214	..	235 455	5	15
18	,, (,,), .	97 = 207	100 = 212	191 - 214	..	228 - 442	4	30
19	,, (,,), .	97 = 207	..	101 214	..	235 455	4	55
20	Cotton, . . .	139 = 282	..	..	..	200 = 392	1	4
21	Olive, . . .	99 = 210	101 = 214	102 = 216	103 = 217	113 = 235	4	30
22	Mixture of 50% of No. 20 and 50% of No. 21	102 = 216	117 = 243	..	..	200 = 392	1	29
23	Mixture of 25% of No. 20 and 75% of No. 21	99 = 210	105 = 221	112 - 234	..	200 = 392	1	52
24	Mixture of 10% of No. 20 and 90% of No. 21	99 = 210	102 = 216	105 - 221	127 = 261	200 = 392	2	9

The following results with the same sample of pure cottonseed oil were obtained on first using one of Mackey's testers :—

Experiment Number.	Temperature (° C.) after the Expiration of Minutes.							
	60	75	81	84	90	92	105	109
1	100°	122°	200°	250°	...	...	...	...
2	99°	102°	...	...	107°	...	165°	250°
3	100°	111°	...	...	225°	250°	...	...
4	102°	125°	...	...	250°	...	...	...
5	101°	120°	...	...	250°	...	...	...

In experiment No. 2 the temperature did not at first rise so rapidly as in the others, but it shot up rapidly after a time, and reached 250° in about 1¾ hours. In this experiment, the wool was teased out with perhaps over-extreme care ; in the last two experiments less care was taken.

An observation may here be mentioned which, though not strictly bearing on lubricants, is of importance to users of this apparatus. Some linseed oil varnish containing 58 per cent. of oil of turpentine, which was believed to have caused a fire, was being tested, but at first no heating effect could be obtained. The temperature of the mixture of 14 grms. of varnish and 7 grms. of wool rose to 100° in twenty-eight minutes, but remained stationary at 105° for two hours. Every attempt to obtain a different result failed. 14 grms. of a mixture of cottonseed oil and turpentine in the same proportions failed to rise higher than 142° C. in 150 minutes, and 33 grms. of the same mixture (containing 14 grms. of cottonseed oil) did not rise beyond 103°. It became evident that the heavy turpentine vapour filling the inner chamber prevented access of sufficient air to maintain the oxidation. The air-inlet tube B was therefore connected up to an air-supply tap, and a current of air (2 litres per minute) was forced through the apparatus. Repeating the experiment under these conditions, the 33 grms. of the cottonseed oil and turpentine mixture rose to 182° in two hours and to 250° in 123 minutes, and the sample of varnish (containing linseed oil and turpentine) reached 100° C in eighteen minutes and shot up to 250° in thirty-eight minutes.

Since making these observations, we have made a practice of forcing a current of air through the apparatus in testing all oils, and we find the results more regular and reliable. We have also improved the apparatus by replacing the spout shown in the figure by a tube which can be connected to a reflux condenser. This prevents the water in the jacket from boiling to dryness, an event which otherwise is not unlikely to occur.

Q.—DETECTION AND DETERMINATION OF ARACHIS OIL IN OLIVE OIL.

Arachis or earthnut oil so nearly resembles olive oil in general characters that the ordinary physical and chemical tests fail to detect its presence. The chief difference lies in the iodine values, which range as under :—

	Lowest.	Highest.
Arachis oil,	83·3	105
Olive oil,	76·2	91·7

Whilst a high iodine value (say over 87 per cent., which is seldom exceeded by genuine olive oil) might, therefore, be due to the presence of arachis oil, a normal value is compatible with the presence of this oil in considerable proportion,

Arachis oil, however, contains from 4·3 to 5·4 per cent. of arachidic and lignoceric acids ($C_{20}H_{40}O_2$ and $C_{24}H_{48}O_2$), which, owing to their sparing solubility in cold alcohol, can be isolated without much difficulty. Olive oil contains not more than traces of these acids. Upon this difference in composition, Renard has based the following process for the detection and determination of arachis oil, which is here described with some modifications in detail introduced by one of the authors.[1]

10 grms. of the suspected oil are saponified in a basin, as directed in E I. (p. 225), using 8 c.c. of 50 per cent. caustic soda solution and 70 c.c. of alcohol, boiled down gently to about 20 c.c., rinsed with hot water into a separating funnel, decomposed with hydrochloric acid in excess, and shaken with ether to extract the fatty acids. After distilling off the ether in an 8-oz. wide-necked flask, the fatty acids are dried by heating the flask on a steam-bath and sucking out the vapour, and are then dissolved by pouring 50 c.c. of rectified alcohol (sp. gr. 0·834) into the hot flask.

To the solution, which should not be hotter than 110° F., and must not be allowed to cool below 100° F., lest crystals of arachidic and lignoceric acids should separate, 5 c.c. of a 20 per cent. aqueous solution of lead acetate are added, which will precipitate the whole of the arachidic and lignoceric acids as lead soaps, together with some palmitate and oleate of lead.[2] After cooling to about 60° F. and allowing to stand for about half an hour, the alcoholic liquid is decanted through a filter, and the lead soaps are extracted with ether until the washings when shaken in a test-tube with H_2S-water give no colour, or only a slight brown ; the soluble lead oleate is thus removed. It is best not to attempt to wash with ether more than once on the filter, but to rinse the soaps back into the flask and digest with ether, then again filter and again rinse back, using the same filter each time. After doing this about four times, all the lead oleate will have been dissolved out. Washing on the filter takes a much longer time.

The filter paper containing the lead arachidate, etc., is opened in a large plain funnel placed in the neck of a separating funnel, and, before the soaps have had time to dry, they are rinsed into the separator with a jet of ether from a washing bottle. The soaps which adhere to the paper and flask may be decomposed and transferred by rinsing with warm dilute hydrochloric acid, followed by ether. About 20 c.c. more hydrochloric acid (1·10 sp. gr.) are poured into the separator, shaken well to decompose the lead soaps, then run off, and the ethereal solution of the fatty acids is washed with small quantities of water until the lead chloride is removed. The ether is distilled off in an 8-oz. flask, and the residual fatty acids are heated in the water-oven until dry. They are then dissolved by warming with 50 c.c. of 90 per cent. ethyl alcohol (sp. gr. 0·8340), and the solution is cooled to 15° C., when arachidic and lignoceric acids, if present, will crystallize out, either at once or after standing a short time. The flask should be closed by a cork carrying a thermometer.

[1] *Jour. Soc. Chem. Ind.*, xvii. (1898), p. 1124.

[2] This quantity of lead is sufficient for 10 grms. of oil. If more be added, a larger precipitate is produced, containing more lead oleate, which takes more washing out with ether, but no more arachidic and lignoceric acids are obtained ; in fact, if excess of lead be used, as recommended by some chemists, the quantity of these acids recovered is even less, probably owing to the solvent action of the solution of lead oleate in ether on the other lead soaps.

According to Tortelli and Ruggeri,[1] a rough estimate of the amount of earthnut oil present may be made at this stage by observing the temperature at which the crystals commence to form.   For this purpose the liquid in the flask must be heated until the crystals have redissolved, and then allowed to cool slowly.

TABLE LXXXVI.

Temperature at which the crystals commence to form. °C.	Earthnut Oil, per cent.
35–38	100
31–33	60
28–30	50
25–26	40
22–24	30
20·5–21·5	20
18–20	10
16–17	5

In order to determine the proportion of earthnut oil more accurately, the liquid is allowed to stand for one hour,[2] with occasional agitation, at 15° C. or 20° C., or at some intermediate temperature which is nearest to that of the laboratory ; the crystals are then collected on a small filter placed over a 100 c.c. cylinder, using the filtrate alone to rinse out the flask, and are washed several times with small quantities of 90 per cent. alcohol until the filtrate and washings measure 70–80 c.c., unless the quantity of crystals obtained is very small, in which case less may be used.[3]   The filtrate and washings with 90 per cent. alcohol must be measured.   The crystals are then washed thoroughly with 70 per cent. alcohol (sp. gr. 0·8898) in which arachidic and lignoceric acids are quite insoluble.   These washings are not measured, but the washing is continued until a few c.c. of the filtrate remain clear when diluted with water in a test-tube, showing that all soluble fatty acids have been washed out.   The washed crystals are then dissolved off the filter with boiling ether, distilled down in a tared flask, and dried in the water-oven until constant in weight, for which one hour or less usually suffices.   Finally, the melting-point is determined by capillary tube, or preferably by Bensemann's method (p. 203), and the point of incipient fusion should not be lower than 71° C.

Instead of weighing the crystals at this stage, Tortelli and Ruggeri recommend redissolving them in 50 c.c. of 90 per cent. alcohol, recrystallizing for

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[1] *Analyst*, xxiii. (1898), p. 273.

[2] Tortelli and Ruggeri say three hours, but Archbutt's experiments show that one hour is enough.

[3] It is a good plan to do this washing with three separate quantities of alcohol, either 10 c.c. or 5 c.c. each, according to the size of the precipitate, and, after collecting the washing each time in a small beaker, to pour it back through the filter two or three times, so as to thoroughly saturate it before adding it to the main filtrate.   Obviously, this must be done at the same constant temperature as that at which the crystallization took place.   A paper filter may be used, but a Gooch filter used with moderate suction is better, because the crystals can be more completely separated from the mother liquor.

one hour at the same temperature as before, again filtering and washing, first with 90 per cent. and then with 70 per cent. alcohol, and then weighing. The crystals from pure earthnut oil, when thus purified, melt, by Bensemann's method, at $72 \cdot 3°$–$73 \cdot 3°$ C.[1] This recrystallization is not, however, necessary, unless the melting-point of the first crop is too low, or the quantity of crystals large.

As the mixed acids are slightly soluble in the 90 per cent. alcohol used for recrystallization and washing, a correction must be made, which varies according to the weight of mixed acids obtained (*Tortelli* and *Ruggeri*). This correction is given by the following table:—

TABLE LXXXVII.

Weight of Mixed Acids obtained. Grm.	Correction (grm.) to be added per 100 c.c. of 90 per cent. alcohol used, at		
	15° C.	17·5° C.	20° C.
0·9 and upwards.	0·071	0·081	0·091
0·8	0·070	0·080	0·091
0·7	0·069	0·079	0·090
0·6	0·067	0·077	0·088
0·5	0·064	0·074	0·085
0·4	0·061	0·070	0·080
0·3	0·055	0·064	0·074
0·2	0·048	0·056	0·064
0·1 and less.	0·033	0·039	0·046

The percentage of mixed arachidic and lignoceric acids thus isolated from pure earthnut oil by Renard, De Negri and Fabris, Tortelli and Ruggeri, and Archbutt, has varied from 4·28 to 5·40 per cent.; averaging about 4·3 per cent. Therefore, the weight of mixed acids obtained, multiplied by 21, is approximately equal to the weight of arachis oil in the quantity of oil taken for experiment.

The results in Table LXXXVIII. (p. 287) show the degree of accuracy attainable by this method. 10 grms. of oil were taken for the analysis in each case, and the mixed acids were not recrystallized.

The correctness of the method has also been proved by Renard, by De Negri and Fabris, and by Tortelli and Ruggeri. The latter chemists, working on 20 grms. of oil and recrystallizing the mixed acids, obtained the following results:—

Arachis oil taken, per cent.,	.	.	60	50	40	30	20	10	5
Arachis oil found, per cent.,	.	.	60	50	40	31	22	11	6·7

* Reimer and Will found in rape oil an acid of high melting-point, sparingly soluble in alcohol, which they believed to be behenic acid, $C_{22}H_{44}O_2$. Ponzio subsequently identified this acid as arachidic; but

[1] Tortelli and Ruggeri found the melting-point of the recrystallized acids, determined by capillary tube, between 74° and 75·5° C.

judging by the solubility in alcohol and the melting-point, it is probably a mixture of arachidic and lignoceric acids. Archbutt has isolated these acids from 33 out of 51 samples of commercial rape oil, and has proved that the quantity present may amount to as much as 1·43 per cent. He has also found the same acid in mustard oil.[1] It appears from these results that the fact of finding arachidic acid in olive oil is not conclusive proof of the presence of earthnut oil, unless rape and mustard oils are proved to be absent by other tests, of which the saponification value is the most important. Unless the saponification value of a sample of olive oil is below 19·0, neither rape nor mustard oils are likely to be present.

TABLE LXXXVIII.

Composition of the Oil per 100 parts.		Volume of 90% Alcohol. Temperature. Solubility Coefficient.	Mixed Arachidic and Lignoceric Acids.					Arachis Oil found, per cent.
Pure Olive Oil.	Pure Arachis Oil.		Dissolved in the Alcohol.	Weighed	Total.	Per cent.	Melting-point by Capillary Tube °C.	
	100	80 c.c. 15° C. ·063	·0504	·4480	·4984	4·98	71°	100
90	10	73 c.c. 15° C. ·033	·0241	·0265	·0506	·506	71°	10·2
80	20	73 c.c. 15° C. ·033	·0241	·0715	·0956	·956	71°	19·2

R.—COLOUR REACTIONS.

Most of the colour reactions which formed such a prominent feature of the older works treating of oil analysis have been shown to be caused, not by characteristic constituents of the oils themselves,

[1] *Jour. Soc. Chem. Ind.* xvii. (1898), p. 1009.

but by impurities which are more or less perfectly removed in the processes of refining; and many of these reactions, based upon tests made with a limited number of specimens of oil, have been found by more extended experience to be valueless. Although the quantitative methods developed during recent years have made us much less dependent than formerly upon colour tests, the means of identifying oils in mixtures are still imperfect, and such colour reactions as are undoubtedly produced by natural constituents of particular oils, of which there are a few, are valuable.

I. Reactions of Cottonseed Oil.

(a) **The Halphen Reaction.**—Oils containing cottonseed oil, if heated with carbon disulphide, free sulphur, and amyl alcohol, develop a characteristic rose-red coloration, the depth of which is in proportion to the amount of cottonseed oil present. The relative proportions of oil and reagents, and the method of heating, may be varied without interfering with the test, as is evident from the different directions given by different analysts. The following method will be found quite satisfactory :—

3 c.c. of the oil, 1 c.c. of a 2 per cent. solution of sulphur in carbon disulphide, and 1 c.c. of amyl alcohol, are mixed in a small test-tube, which is then heated in a bath of boiling water. With as little as 5 per cent. of cottonseed oil present, a distinct rose-red coloration is developed in from fifteen to thirty minutes; the colour is more intense and more rapidly produced the larger the proportion of cottonseed oil. Less than 5 per cent. can be detected if the heating be continued for one hour, and if the colour be then compared with that of a pure sample of oil tested at the same time.

This is the simplest and best reaction for the detection of cottonseed oil. So far as is known, the only other commercial oil which gives the reaction is kapok oil (Milliau, *Comptes Rendus*, 1904, 807), which would be equally objectionable in a lubricant. Nevertheless, too much reliance must not be placed on this or any other colour test. Thus, it has been found that cottonseed oil which has been heated to 240° C., or even to 150° C., if heated long enough, no longer responds to Halphen's test. It has also been observed that the fat of animals which have been fed on cottonseed cake may give the colour reactions of cottonseed oil, though none has been added (see *Silver Nitrate Test*). Thus, lard oil from the fat of pigs fed on cottonseed cake might be unjustly condemned if conclusions were drawn from the colour reaction alone. Hence, it is evident that these reactions should only be used as adjuncts to other tests, and no conclusions should be drawn from them, unless confirmed by the results of the quantitative reactions.

(b) **The Silver Nitrate Test.**—This test, originated by Becchi, depends upon the presence in cottonseed oil of a substance which reduces silver nitrate. If the oil be saponified and the fatty acids

isolated, they give the same reaction. In Becchi's test, the oil is heated with a complex reagent containing an alcoholic solution of silver nitrate, ether, nitric acid, amyl alcohol, and rape oil; but it is preferable to employ for the test a solution of the fatty acids in pure alcohol, as proposed by Milliau, omitting the amyl alcohol and rape oil. The following method of procedure is recommended :—

Approximately 5 grms. of the oil are saponified as directed in E I. (p. 225). The alcoholic soap solution, concentrated to about 10 or 15 c.c., is diluted with hot water, rinsed into a separating funnel, decomposed with excess of dilute sulphuric acid, and shaken with about 70 c.c. of ether to dissolve the fatty acids. After drawing off the aqueous liquid, the ethereal solution is washed four or five times with small quantities of cold water and poured into a flask. The ether is then distilled off, and the flask containing the fatty acids is heated on a steam-bath for a few minutes to evaporate the remaining traces of ether and water.

The fatty acids thus obtained are immediately dissolved by pouring 20 c.c. of absolute alcohol into the flask, and the solution is poured into a dry test-tube measuring 8 inches × 1 inch. The contents of the test-tube are raised to boiling by cautiously heating over a small Bunsen flame, and then, whilst holding the test-tube over a white tile, 2 c.c. of a 30 per cent. aqueous solution of silver nitrate are added from a pipette. In the presence of 5 per cent. of cottonseed oil, a characteristic brown turbidity is produced almost immediately. The reaction is more rapid and intense the greater the proportion of cottonseed oil present. If there be no immediate reduction, the solution is kept under observation for a minute or two at boiling-point, by moving the tube to and fro from the tile to the flame, and if only 2 per cent. of cottonseed oil be present a distinct reaction, though more slowly developed, will be obtained.

This reaction has been examined by a large number of chemists and found to be characteristic of cottonseed oil. Milliau states, however, that kapok oil gives the same reaction. Some genuine rape oils appear to reduce the silver very slightly, but the reaction takes place slowly, and the colour produced is blackish, whilst with cottonseed oil it is brown. Possibly in these cases the precipitate is sulphide of silver, due to sulphur in the rape oil. In testing fats which have been exposed to the air, or have become rancid, it must be remembered that aldehydic bodies formed by oxidation may reduce the silver solution. Thus Bevan [1] found that lard which had been exposed to the air for some days gave Becchi's reaction, whilst some of the same lard taken from the interior of the mass had no reducing property. Hehner [2] states that genuine butter made from the milk of cows fed largely on cottonseed cake frequently gives the reaction of cottonseed oil.[3]

Since it is not known whether all samples of cottonseed oil reduce

[1] *Analyst*, xix. (1894), p. 88.   [2] *Ibid.*, p. 89.
[3] Confirmed later by experiments made on behalf of the Board of Agriculture. See *Analyst*, xxiii. (1898), p. 255. Soltsien and others have also shown that American lard from pigs fed on cottonseed meal gives a strong colour reaction with the silver nitrate test and with Halphen's test; *Analyst*, 1902, 95, and 1903, 80.

silver nitrate to the same extent, it is not safe to draw quantitative conclusions from this test; but an estimate of the proportion of cottonseed oil based upon the result of the colour test generally agrees fairly well with that calculated from the quantitative results.

Some chemists have obtained good results by the Milliau test, others have formed an unfavourable opinion of it. This different experience may be due to the fact that the fatty acids if kept heated even to 100° C., and especially if washed with boiling water, gradually lose their reducing property.

Thus, the fatty acids obtained from a mixture of rape oil with 5 per cent. of cottonseed oil, which reduced silver nitrate immediately when first tested, completely lost the property by heating in the water-oven for one hour. 50 grms. of pure cottonseed oil were saponified and the fatty acids were obtained. After transferring 5 c.c. to a test-tube, the remainder of the acids were placed in the water-oven in a wide beaker, and at intervals of one hour 5 c.c. were taken out and transferred to tubes. The different quantities were then tested together and the amount of reduction compared. The fatty acids which had not been heated reduced the silver very strongly, the remaining quantities had a reducing power which diminished progressively according to the length of time they had been heated, and after heating for nine hours it was estimated that about 95 per cent. of the reducing action had been lost.

A more rapid loss of the reducing property occurred when the fatty acids were repeatedly boiled with water. Thus, some fatty acids from pure cottonseed oil, which reduced silver very strongly, were boiled with water for one hour in a basin ; the reducing property, though still strongly marked, had decidedly diminished. The same fatty acids were then boiled four times successively, for only one or two minutes each time, with fresh quantities of water, when they were found to have lost from 85 to 90 per cent. of their original reducing power.

From these results it is evident that if the fatty acids for the Milliau test are prepared in the ordinary way, viz., by acidifying the hot soap solution in a basin, heating until the fatty acids are clear, washing with hot water and drying in the water-oven, erratic results may be expected. But by separating the fatty acids with ether in the manner described on p. 289, and by avoiding more than ten to fifteen minutes' heating to expel the ether, the results are more reliable.

Cottonseed oil, however, which has been heated to 240° C. no longer responds to either Becchi's or Milliau's tests.

(e) **The Nitric Acid Test.**—This test is given in the form recommended by Lewkowitsch.[1] A few c.c. of the oil are vigorously shaken in the cold with an equal volume of nitric acid of sp. gr. 1·375 and then allowed to stand. ' If cottonseed oil be present, a characteristic coffee-brown coloration develops in a short time. Stronger acid gives less definite results.

In applying this test to a sample of oil, the colour obtained should be compared with that given under the same conditions by a pure

sample of the same kind of oil. The test is most useful in the case of olive oil which, when pure, is scarcely changed in colour by the nitric acid. In consequence of an observation by Holde that refined rape oil when shaken with nitric acid of 1·41 sp. gr. also gives a brown colour, Lewkowitsch mixed a large number of samples of olive oil with varying proportions of cottonseed oil. on the one hand and rape oil on the other, and shook them with nitric acid of 1·375 sp - gr. After standing for twenty-four hours, the two sets showed striking differences of colour ; those containing cottonseed oil were of a pale brown colour, whilst those mixed with rape oil became more yellowish. In a similar series of tests made by one of the authors it was found, with one sample of rape oil, that although no brown colour was developed within forty minutes, whilst the mixtures containing 5 per cent. and upwards of cottonseed oil all gave a distinct brown colour in the same time, on longer standing the mixtures containing rape oil also became brown in colour, and, before the end of twenty-four hours, could not be distinguished in shade from those containing cottonseed oil. Another sample of refined (Stettin) rape oil, undoubtedly genuine, when mixed in the proportion of 20 per cent. with the same sample of olive oil as was used in the above tests, gave a brown colour in forty minutes which could not be distinguished from the colour given by 20 per cent. of cottonseed oil. A more extended experience has confirmed the fact that many genuine rape oils give a brown colour when shaken with nitric acid of 1·375 sp. gr.

Some genuine lards have been found to give a brown colour with nitric acid ; but this should not mislead an experienced analyst, as the presence of cottonseed oil ought not to be certified unless it is confirmed by quantitative tests, such as the iodine value of the sample. The reaction with nitric acid has this advantage over Halphen's and the silver nitrate tests, that the brown colour is obtained with cottonseed oil which has been heated to 240° C., as well as with oil which has not been heated. Lewkowitsch states, however, that some American cottonseed oils which he has met with gave such a faint coloration with nitric acid that 10 per cent. could not be detected in olive oil by this test ; but such oils are rare.

It may be noted that blown oils, both rape and cotton, even if present to the extent of only 10 per cent., give a very intense red-brown colour when shaken with nitric acid.

II. Reaction of Sesamé Oil.

The Baudouin Reaction.—Sesamé oil contains a substance which produces a rose-red coloration when the oil, either pure or in admixture with other oils, is shaken with a solution of cane sugar in hydrochloric acid.

In making the test, 0·1 grm. of pure cane sugar is first dissolved in 5 c.c. of cold, strong hydrochloric acid (1·16 sp. gr.) ; 10 c.c. of the oil are then added,

the tube is corked, shaken for ten minutes, and allowed to stand. If only 2 per cent. of sesamé oil be present, the acid which separates will be pink in colour. If 5 per cent and upwards be present there will be no need to shake for ten minutes, as the emulsion will be observed to become pink while it is being shaken.

Several observers have found that in the case of certain olive oils of undoubted purity the acid liquid assumes 'after a short time' a violet coloration. Villavecchia and Fabris[1] further state that some genuine Italian olive oils give a rose coloration similar to that produced by sesamé oil. We have confirmed this latter observation in testing a few genuine olive oils, but the pink colour observed by us has always been very faint. If, after ten minutes' shaking, the acid which separates is not distinctly pink or red in colour, sesamé oil should be assumed to be absent, and no notice should be taken of any colour which develops on standing. In any case, error is not likely to occur so long as the results of this test are supported by the results of the quantitative reactions. Millian has found that if the test be applied to the fatty acids instead of to the oil, any possible error is obviated, and this has been confirmed by other chemists.[2] Therefore, Milliau's method should be adopted in any case where doubt exists as to the cause of the coloration. Villavecchia and Fabris[3] find this colour reaction to be due to *furfurol*, produced by the action of hydrochloric acid on sugar, and they have accordingly proposed to employ a solution of furfurol instead of cane sugar. As furfurol itself gives a violet coloration with hydrochloric acid, a very minute quantity must be used.

For the test, a 2 per cent. solution of furfurol in alcohol is prepared. 0·1 c.c. of this solution is placed in a test tube ; 10 c.c. of hydrochloric acid (1·16) and 10 c.c. of the oil are added ; the tube is then corked, shaken for half a minute, and allowed to stand. If even 1 per cent. of sesamé oil be present, the acid which separates has a pink coloration ; with 5 per cent. a strong rose-red colour is obtained. This test is recommended, as it is simpler than the test with sugar, and half a minute's shaking is quite sufficient.

III. Reactions of Cholesterol and Phytosterol.

. (a) **With Chloroform and Sulphuric Acid** (*Hesse, Salkowski*).—If a few centigrammes of cholesterol be dissolved in 2 c.c. of chloroform and the solution be shaken with an equal volume of sulphuric acid of 1·76 sp. gr., the chloroformic layer at first becomes pink, deepening more or less rapidly (according to the quantity of cholesterol present) to blood-red; then cherry-red or purple, the latter colour persisting for

[1] *Jour. Soc. Chem. Ind.*, xii. (1893), p. 67.
[2] *Ibid.*, xvii. (1898), p. 275. The olive oils of Tunis are said to frequently give a red or rose coloration with the Baudouin test, but the fatty acids do not. See *Chem. Trade Journal*, 1902, 524.
[3] *Ibid.*, xiii. (1894), p. 69.

some time and changing to a mahogany tint on prolonged standing. If some of the purple solution be poured into a porcelain basin, the colour soon fades to a dirty green and ultimately yellow, but the crimson or purple tint is restored on agitating again with strong sulphuric acid. The strength of the sulphuric acid used in this test is important, and a comparative experiment should be made with pure cholesterol. A crimson or purple colour is developed, though slowly, with as little as 5 milligrms. of cholesterol in 2 c.c. of chloroform. Salkowski states that the sulphuric acid which separates shows a strong green fluorescence. With p~re cholesterol (probably from gall-stones) and sulphuric acid of 1·1   ~ gr., we have been unable to obtain more than a faint fluorescer   d that only after standing for a day or two. Lewkowitsch l   'A that the green fluorescence is caused by the presence of isocho,

(*b*) With **Acetic Anhydride and Sulphuric Ac**   *ermann*).—If to a cold solution of cholesterol in acetic anhydrid\   ntrated sulphuric acid be added, drop by drop, without shakin,   et coloration, quickly changing to blue, is produced where the   ids meet. On shaking, the whole liquid becomes deep blue, slowly   nging to green or bluish-green. This reaction is very delicate, and 's given by less than 1 milligrm. of cholesterol in 2 c.c. of acetic anhydride. Isocholesterol gives the same reaction (*Schulze*). A violet or violet-red coloration is given also by solutions of colophony and rosin oil in acetic anhydride, but in these cases the colour (which is produced by *one drop* of sulphuric acid and shaking) does not change to blue, but either fades slowly to a neutral tint or (if heated) changes to a brown or yellow colour.

(*c*) **With Nitric Acid** (*Schiff*).—A crystal of cholesterol heated with a drop of concentrated nitric acid and slowly evaporated leaves a yellow spot which is turned red by ammonia. Isocholesterol gives the same reaction (*Schulze*).

(*d*) **With Hydrochloric Acid and Ferric Chloride** (*Schiff*).—If a little cholesterol be triturated with a drop of a mixture of 5 vols. strong hydrochloric acid and 1 vol. of ferric chloride solution, and slowly evaporated to dryness, the particles which have remained undissolved assume a violet-red colour, changing to blue. Some other substances, such as oil of turpentine and camphor, behave in the same way. Isocholesterol does not give this reaction.

IV. Detection of Rosin Oil.

(*a*) **The Liebermann-Storch Reaction.**[1]—If a small drop of rosin oil be dissolved in 2 or 3 c.c. of cold acetic anhydride and *one drop* of sulphuric acid of sp. gr. 1·53 be added to the liquid and shaken, a characteristic violet-red coloration is produced, becoming redder,

[1] *Jour. Soc. Chem. Ind.*, vii. (1888), pp. 135, 136.

then brown or greenish-brown. This reaction is given even by highly-refined rosin oil.

To detect rosin oil in mineral oil, 2 c.c. of the sample are shaken for a minute or two in a dry test-tube with about 3 c.c. of acetic anhydride at a gentle heat and allowed to separate. After cooling, the acetic anhydride is drawn off with a fine pipette and transferred to another tube, or, preferably, the liquid is poured on to a small filter previously moistened with acetic anhydride, when the oil will remain on the filter and a bright filtrate will be obtained. To this filtrate one drop of sulphuric acid of sp. gr. 1·53 is added, and in the presence of rosin oil an immediate, very fugitive coloration, varying from violet-red to cherry-red, is obtained. Pure mineral oil gives a yellow or brown colour, which is sometimes so dark as to obscure the rosin oil reaction. In such cases, the test may be made more delicate by pouring one drop of the acetic anhydride filtrate into another tube before adding sulphuric acid ; on diluting this with 1 or 2 c.c. of acetic anhydride and adding one drop of sulphuric acid to the diluted liquid, the violet coloration is more plainly seen. Five per cent. of rosin oil may be thus detected. Morawski points out that the dark coloration of mineral oil with sulphuric acid is intensified by the application of too much heat in shaking the oil with acetic anhydride, and that if the extraction be done in the cold a paler colour will be obtained and the rosin oil reaction will be less obscured.

Owing to the fact that cholesterol and phytosterol also give a violet coloration with sulphuric acid in acetic anhydride solution, Storch has stated that this test cannot be relied upon for the detection of rosin oil in the presence of fatty oils ; but Morawski has found that the test is applicable to most vegetable oils, which, when pure, give only green, yellowish, or yellowish-brown colorations. If, therefore, the presence of rosin oil in a fixed oil be suspected, the coloration obtained should be compared with that yielded under similar conditions by a pure sample of the same fixed oil. In the case of oils such as shark-liver and others which, owing to the presence of cholesterol, do interfere with the test, Lewkowitsch suggests that the oil should be saponified, and after extraction of the unsaponifiable matter (including cholesterol) with ether, the fatty acids liberated from the soap solution should then be tested for rosin acids, which always accompany rosin oil. If the sample under test contains added rosin or rosin soap, this device of course fails ; rosin oil must then be searched for in the unsaponifiable matter by other tests.

(*b*) **Holde's Test.**—According to Holde,[1] if 5 c.c. of oil be vigorously shaken in the cold with 5 c.c. of sulphuric acid (1·60 sp. gr.) the acid layer which separates assumes a distinct red colour in the presence of rosin oil. The vegetable and animal oils and most mineral lubricating oils impart only a faintly yellow to yellowish-brown or grass-green colour to the acid. Various kinds of fish oil, imperfectly refined mineral oils, also tar oil, cause a dirty brown-red coloration of the acid ; and, in such cases, the detection of rosin oil by means of this reaction is only made possible by extracting it with 90 per cent. alcohol and mixing the alcoholic extract in a test-tube with a small quantity of sulphuric acid of 1·53 sp. gr., which is allowed to flow down the side of the tube.

c·Untersuchung der Schmiermittel, p. 115.

Holde states that 1 per cent. of rosin oil can be detected by this reaction, but our experience is that the test is decidedly less delicate than the Liebermann-Storch reaction. Pure rosin oil certainly gives a very characteristic bright red colour, which distinguishes it at once from pure mineral oil, but comparative experiments with pure mineral oil and mixtures of the same with rosin oil in different proportions showed that the mixture containing 5 per cent. of rosin oil gave only a very slightly redder colour than the mineral oil alone. The difference was distinct with 10 per cent., and still more so with 20 per cent. of rosin oil, but the reaction could not be depended upon for the detection of 10 per cent., except by making a blank experiment simultaneously with the pure mineral oil. Shark-liver oil and seal oil gave a red-brown colour, as stated by Holde. Refined rape oil scarcely coloured the acid, but with blown rape the whole mixture became nearly black in colour and the acid could not be distinguished from the oil.[1]

V. Detection of Rosin Acids (Rosin).

The Liebermann-Morawski Reaction.—If a few milligrms. of colophony be dissolved, by warming, in 2–3 c.c. of acetic anhydride and the solution be made quite cold, on adding *one drop* of sulphuric acid of 1·53 sp. gr. and shaking, a pure violet colour is produced, slowly fading to a neutral tint. With concentrated acid the colour is redder, and if the liquid be heated (*e.g.* by adding several drops of acid as in testing for cholesterol) the colour changes to brown or yellow.

To detect rosin in an oil, fat, or grease by means of this reaction, the substance should first be saponified and the soap solution shaken with ether to remove unsaponifiable matters, especially rosin oil and cholesterol. The fatty acids are then obtained from the soap solution and a small portion is dissolved in acetic anhydride in the cold, or at a very gentle heat. The solution having been made quite cold, sulphuric acid of sp. gr. 1·53 is allowed to flow down the side of the tube, and in the presence of rosin acids a coloration varying from violet to violet-red is produced where the liquids mix. Lewkowitsch recommends this test as thoroughly trustworthy in all cases.

8.—DETECTION AND DETERMINATION OF ROSIN OIL IN MINERAL (UNSAPONIFIABLE) OIL.

(*a*) **The Liebermann-Storch Colour Test.** (See p. 293).

(*b*) **The Acetone Test.**—According to Demski and Morawski,[2] rosin oils mix with acetone in nearly all proportions, whilst mineral oils require several times their volume of acetone to effect complete

[1] See also Holde, *Jour. Soc. Chem. Ind.*, ix. (1890), p. 419, and Grittner, *ibid.*, x. (1891), p. 728.
[2] *Dingl. polyt. Jour.*, cclxiii., p. 82

solution.[1] If, therefore, an unsaponifiable oil gives a clear solution
with an equal volume of acetone, it is either a pure rosin oil or a
mixture of this with very little mineral oil; if an insoluble residue
remain, it consists of mineral oil. Wiederhold,[2] who has proposed
the same test, states that the acetone must be dry and free from acid,
but that the presence of aldehyde is of no importance. The difference
between the solubility of rosin oil in moist and in dry acetone is very
considerable. Rosin oil will dissolve in half its volume of *dry* acetone
at 15° C.

(c) **Finkener's Test.**—Finkener[3] has proposed the use of a solvent
prepared by mixing at 15·5° C., 10 volumes of alcohol of sp. gr.
0·8182 with 1 volume of chloroform. Rosin oil dissolves in from 10
to 12 volumes of this mixture at 23° C., whilst mineral oils are not
completely soluble even in 100 volumes. Occasionally rosin oil is
met with which, when dissolved in 10 volumes of the mixture and
allowed to stand for several hours at 23° C., deposits an oily sedi-
ment amounting to from 3 to 7 per cent. of the rosin oil taken, but
if 12½ volumes of the mixture be used instead of 10 volumes, any
insoluble residue then obtained may be assumed to be mineral oil.
Wiederhold[4] considers that the necessity of working at 23° C. renders
the above test impracticable, and he states that if 16 volumes of the
chloroformic alcohol be used the test may be made at a temperature
of 15° C.

(d) **Polarimetric Test.**—According to Valenta, most rosin oils
are strongly dextro-rotatory, the rotation varying from 30° to 40°
in a 100 mm. tube. Demski and Morawski observed a rotation of
about 50°. The rotation of seven samples examined by Pelgry at the
Charlottenburg Versuchsanstalt varied from 32° to 42°.[5] On the
other hand, pure mineral oils are, as a rule, optically inactive, one
sample only having been found to give a rotation of + 1·2°. Dark
coloured oils must be decolorized by filtration through animal
charcoal.

(e) **Determination of Rosin Oil by Valenta's Method.**[6]—Glacial
acetic acid at 50° C. dissolves rosin oil much more freely than
mineral lubricating oil. Thus, Valenta found that 100 grms. of
glacial acetic acid dissolved at 50° C., from ten different samples of
mineral oil experimented with, quantities ranging from 2·67 to 6·50
grms.; whilst the same quantity of glacial acetic acid dissolved 16·88
grms. of rosin oil. Walker and Robertshaw[7] similarly found the
solubility of a sample of mineral oil in 100 grms. of glacial acetic

[1] Borneo mineral oil of sp. gr. 0·97 to 0·99 is readily soluble in an equal volume
of acetone. It does not, however, give the Liebermann-Storch reaction. (Jenkins)
Analyst, 1902, 240.
[2] *Analyst*, xviii. (1893), p. 206; *Jour. Soc. Chem. Ind.*, xii. (1893), p. 551.
[3] Holde, *Die Untersuchung der Schmiermittel*, p. 116.
[4] *Analyst*, xviii. (1892), p. 207.
[5] Holde, *Die Untersuchung der Schmiermittel*, p. 118.
[6] *Jour. Soc. Chem. Ind.*, 1884, 643.
[7] *Analyst*, 1902, 238.

acid to be 4·4 grms., and of two samples of rosin oil to be, respectively, 16·8 and 16·6 grms., thus confirming Valenta's figures. Upon this difference of solubility Valenta has based the following test :—

2 c.c. of the suspected oil are mixed in a test-tube with 10 c.c. of glacial acetic acid ; the tube is immersed in water at 50° C. and frequently agitated. The acid is then filtered through a damp filter, the second third of the filtrate being collected. A weighed quantity of this is titrated with standard alkali, and the amount of acetic acid calculated. The difference between this weight and that of the quantity taken is the amount of oil dissolved.

Valenta found that the solubility of a mixture of rosin oil and mineral oil was not proportional to the relative quantities of each in the mixture, and, therefore, he did not consider the above a quantitative method. On the other hand, Walker and Robertshaw found that a mixture of equal weights of mineral oil and rosin oil gave 10·84 per cent. of dissolved oil, theory requiring 10·59 per cent. They, therefore, consider this the best method of analysing quantitatively a mixture of mineral oil and rosin oil. Allen has pointed out that errors would be caused by the presence of rosin acids in the rosin oil. He proposed, therefore, to neutralize the greater part of the acetic acid with alkali, dilute with water, and extract the rosin and mineral oil with ether. Probably the best method of procedure in all cases would be first of all to saponify, extract and weigh the unsaponifiable matter (thus freed from rosin acids), and examine this by Valenta's method. The rosin acids, together with fatty acids from any fixed oil present, could be recovered from the soap solution and separately determined.

(*f*) **Determination of Rosin Oil by Storch's Method.**[1]—According to Storch, rosin oil mixes with absolute alcohol in all proportions, but the presence of a comparatively small proportion of water greatly reduces the solubility. Thus, 96 per cent. alcohol dissolves from 11·3 to 16·2 per cent. of rosin oil, whilst 90 per cent. alcohol dissolves only from 2·6 to 4·0 per cent. Mineral oil, on the other hand, is much less soluble than rosin oil. Upon this difference of solubility, Storch has based the following method for the determination of rosin oil when mixed with mineral oil :—

10 grms. of the unsaponifiable oil, which has been proved by the foregoing tests to contain rosin oil, are gently warmed with 50 grms. of 96 per cent. alcohol (sp. gr. 0·8123), then well shaken and allowed to cool. All the rosin oil, even if 50 per cent. be present, will now be dissolved in the alcohol, together with some of the mineral oil. The alcoholic solution having been carefully drawn off with a fine pipette and transferred to a small Erlenmeyer flask about seven cm. high, the surface (only) of the undissolved mineral oil is rinsed with a few c.c. of 90 per cent. alcohol which is also transferred to the flask. The latter is then placed on a water-bath, surrounded by a bottomless beaker, and the alcohol is gently boiled off.

[1] *Jour. Soc. Chem. Ind.*, vii. (1888), p. 136 ; *Analyst*, xiii. (1888), p. 71.

When the residual oil is free from bubbles, it is cooled and weighed. (*Residue A*.) Storch has proved that by evaporating off the spirit in this way the loss of rosin oil is imperceptible; if a beaker be used it is greater, though very small; but in a basin a large loss occurs. Residue *A* is next warmed and shaken, exactly as before, with ten times its weight of 96 per cent. alcohol, *i.e.* with just enough to dissolve it if pure rosin oil, and the solution is again evaporated and the residue weighed. (*Residue B*.) Both residues contained the whole of the rosin oil plus as much mineral oil as the alcohol used could dissolve; but, as in the second extraction less alcohol was used than in the first, an insoluble residue remained, consisting of the mineral oil dissolved by the difference between the two quantities of spirit employed. Knowing the weight of this residue (= wt. of *A* – wt of *B*) and the weight of the alcohol in which it was dissolved, the solubility of the mineral oil can be calculated. The weight of mineral oil in residue *B* is thus found, and the difference is the weight of rosin oil in the 10 grms. of oil taken. Storch found by experiment that this result is a little below the truth, and that the correct result is more nearly the mean between this figure and the weight of residue *B*.

EXAMPLE.

11·22 grms. of mineral oil containing 10 per cent. of rosin oil were taken.

				Grms.		Grms.
1st Extraction,	.	.	Alcohol used,	50·0	Residue *A*,	1·5136
2nd ,,	.	.	,,	15·5	,, *B*,	1·1584
Differences,	.	.	Alcohol,	34·5	Mineral oil,	·3552

Therefore, 34·5 grms. of alcohol dissolved 0·3552 grm. of mineral oil, and therefore 15·5 grms. of alcohol dissolved 0·1595 grm. of mineral oil.

Deducting 0·1595 grm. from the weight of residue *B* leaves 0·9989 grm., or 8·90 per cent. of rosin oil. Residue *B* without this correction is equivalent to 10·32 per cent. The mean value is 9·60 per cent., which is not far from the truth.

(*g*) **Determination by M'Ilhiney's Method.**[1]—This method depends upon the fact that nitric acid, when heated with rosin oil, converts it into a brittle red resin, whilst mineral oil is not much affected. The red resin is insoluble in petroleum ether, in which the mineral oil easily dissolves.

50 c.c. of nitric acid (sp. gr. 1·2) are heated to boiling in a flask of 700 c.c. capacity. The flame is removed and 5 grms. of the oil are dropped in. The flask is then heated on the water-bath, with frequent shaking, for fifteen to twenty minutes; about 400 c.c. of cold water are then added, and the liquid is made quite cold. The unchanged mineral oil is then dissolved by shaking with petroleum ether, which is separated and distilled off in the usual manner, and the residual oil is weighed. As mineral oils lose about 10 per cent. when thus treated, the weight obtained, divided by 0·9, gives the amount of mineral oil in the quantity of oil taken. A mixture consisting of 76 per cent. mineral oil and 24 per cent. rosin oil gave, by this method, 76·8 per cent. of mineral oil.

ur. Amer. Chem. Soc., xvi. (1895), p. 385.

T.—DETERMINATION OF PARAFFIN IN MINERAL OILS.

The following method[1] is due to Holde (after *Engler* and *Böhm*). It will seldom be required, but may occasionally be found useful.

10 to 20 c.c. of oils poor in paraffin (Russian distillates, etc., setting below -5° C.), or 5 grms. of such as are rich in that constituent (American, Scotch, or Galician oils setting at or above 0° C.), are treated, at the ordinary temperature, with a mixture of 98·5 per cent. alcohol and anhydrous ether (1 : 1) until a clear solution is obtained. The liquid is cooled in a freezing mixture of ice and salt to about -20° to -21° C., when more alcohol-ether is gradually added, with thorough agitation, until no oil drops, but only solid paraffin flakes or crystals, remain in suspension, and then, whilst still

cooled to at least 19° to 21° C., the liquid is poured on to a chilled 9 cm. filter paper, previously moistened with the alcohol-ether mixture, which is contained in the apparatus shown in fig. 74. The precipitate is washed with cold (-19° to -21° C.) alcohol-ether (1 : 1; or for soft paraffin 2 : 1) at a temperature as much below -15° C. as possible. In the case of soft paraffin, the temperature should average -18° to 19° at the highest. In washing the precipitate it is repeatedly stirred up, and as soon as 5-10 c.c. of the filtrate leaves on evaporation only a trace of fatty or paraffin-like residue, solid and not oily at the ordinary temperature, the washing is discontinued. If any doubt exists as to the paraffin being thoroughly freed from oil, or if the washing takes too long, the filter should be removed to another funnel, and the contents dissolved into a small flask with the least possible quantity of benzine. After evaporation of the benzine, the paraffin is redissolved in 4 to 5 c.c. of warm ether, which is then mixed with twice its volume of absolute alcohol, vigorously stirred, and cooled to -18° to -20° to reprecipitate the paraffin, which is again filtered and washed, as already described, until free from oil. This reprecipitation is necessary for oils containing much soft paraffin, otherwise so much liquid is used in washing the precipitate that an appreciable quantity of

FIG. 74.—Determination of Paraffin.

paraffin is dissolved. The purified paraffin is finally dissolved into a tared flask with hot benzine or ether, which is distilled off, and the residue is heated on the steam-bath until the smell of benzine or ether has disappeared. The flask is then heated inside the water-oven for a quarter of an hour and weighed when cold. Prolonged heating causes loss of paraffin. The whole
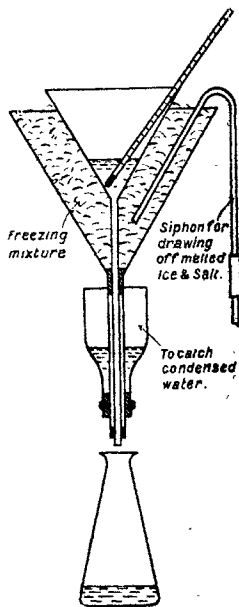
[1] *Jour. Soc. Chem. Ind.*, xvi. (1897), p. 362.

operation occupies from one to two hours. Duplicate results with the same
sample agree within 0·23 per cent. for hard paraffin and 0·33 per cent. for
soft paraffin. Two samples of Russian machine oil yielded 0·34 per cent. and
0·36 per cent. of paraffin, respectively. An American spindle oil, fluid but
thick at +2° C., and which set at 0° C., was found to contain 4·11 per
cent. of paraffin.

U.—ASPHALT AND RESIN IN MINERALS OILS.

Such slight tendency to 'gum' and form sticky or resinous
deposits as is possessed by pure mineral lubricating oils is attributed
by Holde[1] to the presence of dissolved substances of a resinous,
asphaltic, or pitchy nature, which gradually accumulate in and
thicken the oil film, whenever the conditions of working are such
that evaporation of the fluid constituents of the oil can take place.
These substances are composed, chiefly, of carbon and hydrogen, with
small quantities of oxygen and sulphur, and are regarded by Engler
as oxidation products. They occur, chiefly, in the dark-coloured
'reduced' oils; in the processes of distillation and refining to which
the pale oils are subjected they are for the most part eliminated.
Holde divides them into three classes :—

1. **Resins, soluble in 70 per cent. Alcohol.**—These substances,
which are obtained by shaking the oil with 70 per cent. alcohol and
evaporating the solution, resemble colophony in appearance ; but
instead of giving a violet colour in Morawski's test with acetic an-
hydride and sulphuric acid (p. 295), a yellowish-brown or dirty-brown
colour is produced. Some have acid characters and soap-forming
properties ; others are neutral. According to Holde, badly refined
mineral oils may contain as much as 3·5 per cent. of these resins ;
but, as a rule, the proportion does not exceed 0·6 per cent. in pale
oils and 1 per cent. in dark oils. Some of these resins are soluble
in petroleum spirit, others are insoluble, but they all dissolve com-
pletely in alcohol-ether (4 : 3 and also 3 : 4).

2. **Asphalt, insoluble in Petroleum Spirit.**—Bender[2] found that
dark-coloured mineral oils, when dissolved in pceroleum spirit and
allowed to stand, deposit a substance which, when collected, washed,
and dried, is a fine powder resembling dark brown coal in appearance,
having a slightly bituminous smell, and burning with a smoky
flame. This substance dissolves easily in benzene, and is of the
nature of asphalt. Holde finds that the amount of asphalt thus
obtained from mineral oil depends upon the sp. gr. and boiling
point of the petroleum spirit used (being largest with spirit of low
boiling-point) ; upon the relative volume of spirit used (which should
be large) ; and upon the time of standing (which should be at least
twenty-four hours). The asphalt, which usually exists dissolved and

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[1] *Jour. Soc. Chem. Ind.,* xiii. (1894), p. 668 ; and xiv. (1895), p. 894.
[2] *Ibid.,* x. (1891), p. 354.

not suspended in the oil (the suspended particles seen in dark oils being, chiefly, paraffin coloured with asphalt), at first dissolves along with the oil in the petroleum spirit; only on standing does it separate out, and the less there is in the oil the longer it takes to precipitate. Holde states that, except as a colouring agent, the influence of this asphalt at ordinary temperatures is small; but, when the oil is used at temperatures and under conditions in which the fluid hydrocarbons can evaporate, the asphalt and resins, accumulating in the film, cause it to become thick and sticky, and ultimately dry and resinous. The largest amount of asphalt, amounting to 5 or 6 per cent., is found in German (Alsatian and Hanoverian) oils; the smallest quantity is met with in American and Russian oils.

3. **Asphalt-Pitch insoluble in Alcohol-Ether** (4 : 3).—By dissolving dark mineral oils in a mixture of alcohol and ether, Holde has obtained as an insoluble residue this substance, which includes the asphalt precipitated by petroleum spirit, but is much more fusible, resembling soft pitch. The amount obtained from a given oil increases with the proportion of alcohol in the solvent. With the 4 : 3 mixture, the amount of asphalt-pitch obtained from Russian oil ranged from 0·16 per cent. in a distilled machinery oil to 5·7 per cent. in a railway oil; a thick lubricating oil from Oelheim gave 11·1 per cent., and a very thick crude petroleum from Wietze gave 15·4 per cent.

For the detection and determination of these substances, Holde proceeds as follows : —

(a) *Determination of Resins soluble in 70 per cent. Alcohol.*—8–10 c.c. of the oil are well shaken in a test-tube with an equal volume of 70 per cent. alcohol (sp. gr. 0·8898), the mixture being heated. It is then made quite cold. After complete separation has taken place, the alcoholic liquid is drawn off, without loss, and evaporated to dryness in a tared beaker containing a glass rod. When perfectly dry and cold, the consistency of the residue is ascertained by feeling it with the glass rod, and if sufficient in amount to be worth weighing, it is weighed. The quantity of natural resin thus obtained from a pale mineral oil should not, says Holde, exceed 0·3 per cent., and from a dark oil 1·0 per cent. If a quantity notably in excess of these be obtained, the treatment with 70 per c.. alcohol should be repeated until the whole of the resin has been extracted, and after weighing the residue it should be tested by the Liebermann-Morawski reaction in order to ascertain whether colophony has been added to the oil. The addition of colophony would, however, raise the acidity of the oil; 1 per cent. of acidity as oleic acid being equivalent to about 1·24 per cent. of colophony. If, therefore, the acidity of a mineral oil (determined as described on p. 216) be less than 0·1 per cent., not more than 0·12 per cent. of colophony can be present.

(b) *Detection and Determination of Asphalt.*—About 0·5 c.c. of the oil is shaken in a test-tube or small flask with 40–50 c.c. of petroleum spirit boiling below 35° C., and allowed to stand. In the presence of asphalt, dark insoluble flakes appear, either immediately or within twenty-four hours, which, when collected on a filter, resemble asphalt in appearance and, whilst freshly precipitated, dissolve completely in coal-tar benzene.

To determine the amount, from 1·5 to 3 grms. of an oil rich in asphalt, or

from 5 to 20 grms. of an oil poor in asphalt, are dissolved in from 300 to 500 c.c. of petroleum spirit and allowed to stand for at least twenty-four hours, when the greater part of the precipitate will have settled. The clear liquid is then decanted through a small filter-paper, and the precipitate is brought thereon and well washed with petroleum spirit until the filtrate leaves no oily residue on evaporation. The asphalt is then immediately [1] dissolved off the filter by means of pure benzene, the solution is evaporated in a tared dish, and the residue is dried at 100° C. and weighed. Duplicate experiments with the same oil are said to agree within 0·1 per cent., provided the same description of petroleum spirit is used, but not otherwise. For example, an Alsatian oil gave with petroleum spirit boiling between 60° and 80° C. only 2·1 per cent. of asphalt, but the same oil with spirit distilled below 50° C. yielded 5·5 per cent., and with spirit boiling below 41° C., 5·7 per cent. of asphalt.

(c) *Detection and Determination of Asphalt-Pitch.*—If about 0·5 c.c. of the oil be dissolved in 5 c.c. of ether, and 7 c.c. of absolute alcohol be added, both the asphalt and the soft pitch separate in the form of a tenacious deposit which clings to the sides of the glass. This deposit is entirely soluble in benzene. Petroleum spirit dissolves the pitch and leaves the asphalt.

To determine the amount, 1-2 grms. of the oil is dissolved in 30 to 40 c.c. of alcohol-ether (4 : 3) in a well-stoppered flask, and, after well shaking, the flask is allowed to stand for one or two days. The solution is then poured through a small filter, and the flask and filter are well washed with the alcoholic ether until the filtrate leaves no oily residue after evaporation at the ordinary temperature. Then the asphalt-pitch clinging to the sides of the flask, and any that has found its way on to the filter, are dissolved in the least possible quantity of hot benzene, which is evaporated in a tared dish and the residue weighed after drying at 100° C. until constant.

Small quantities of resinous and tarry matter are obtained from most mineral lubricating oils by boiling with alcoholic soda solution, as in the process for determining the amount of saponifiable matter (E, II., p. 228). After the alkaline liquid has been freed from all mineral oil by shaking with ether, if it be acidified and again shaken with ether, and the latter drawn off and evaporated, the resinous matter is obtained as a more or less dark-coloured residue.

V.—CAOUTCHOUC IN MINERAL OIL.

Caoutchouc is sometimes dissolved in mineral lubricating oils to produce a factitious viscosity. In a case investigated by Holde,[2] 2 per cent. of caoutchouc was found to have increased the apparent viscosity of an oil from 21·2 to 117 (*Engler*).[2] The adulterated oil was of an adhesive or tacky nature, pulling up in threads when touched. Tested in a Martens' machine, the coefficient of friction was found to be so high, and the rise of temperature of the bearing so rapid, as to condemn the oil as a lubricant. By dissolving the oil in a mixture of alcohol, 3 parts, and ether, 4 parts, the caoutchouc

[1] If allowed to stand, the precipitate is apt to become less soluble in benzene.
[2] *Die Untersuchung der Schmiermittel,* p. 122.

was left insoluble, and the amount present was determined by collecting the insoluble flakes, washing, drying and weighing them.

W.—DETECTION OF SOAP AND INORGANIC SUB-STANCES IN MINERAL OILS AND GREASES.

For the detection of soap in lubricants, the determination of ash is a valuable guide (see p. 304). As a further test, about 0·5 c.c. of the sample may be shaken with 5–10 c.c. of petroleum spirit (redistilled below 75° C.), until dissolved or thoroughly disintegrated. Two cases then present themselves : --

(a) *A clear solution is obtained.* -Add 1 c.c. of Schweitzer and Lungwitz's reagent (a saturated solution of metaphosphoric acid in absolute alcohol, made by shaking excess of the powdered acid with alcohol in a stoppered bottle).[1] If soap be present, even in traces, a flocculent precipitate will be produced.

This test was specially devised for the detection of small quantities of aluminium soap ('viscom,' 'gelatin') which are sometimes added to mineral oils to produce a factitious viscosity. The reaction depends upon the fact that whilst free metaphosphoric acid is soluble in alcohol and in ether, aluminium metaphosphate and the metaphosphates of the alkalies and alkaline earths are insoluble. The authors of the test have proved by experiments with a large number of fixed oils and fats, mineral oils, rosin oil, vaseline, etc., that if no soap be present no precipitate is obtained in twenty-four hours. Some waxes, however, also ozokerite, are precipitated from their solutions in petroleum spirit by absolute alcohol ; therefore, if pure absolute alcohol (free from phosphoric acid) be found to give a precipitate, the test must be repeated, using ordinary ether as the solvent and a solution of metaphosphoric acid in ether as the reagent.

(b) *An insoluble residue remains.*—Dissolve, if necessary, a larger quantity of the substance in more petroleum spirit, filter through a small filter paper, and wash with petroleum spirit until all soluble oily matter is removed. Then drive off the petroleum spirit by evaporation, transfer some of the dry residue to a small test-tube, and heat it with dilute hydrochloric acid. Soap, if present, will be decomposed, and the fatty acids set free will be seen floating on the liquid, either while hot or after cooling. If the result be uncertain, shake the cold liquid with a little ether, draw off the ether with a pipette, and evaporate it in a watch-glass to detect the fatty acid, which will crystallize on solidification. Resin would be recognized by its physical characters. The base of the soap, whether aluminium, calcium, sodium lead, etc., may be detected by pouring the acid solution through a wet filter and applying the usual tests.

Another portion of the residue insoluble in petroleum spirit may be burnt in a small platinum dish or porcelain crucible. If no ash remain, the insoluble matter was free from soap. If soap be present, an ash consisting of the carbonate or oxide of the metallic base will be obtained.

The residue insoluble in petroleum spirit may contain, besides soap, other substances, such as graphite, soapstone, chalk, lime, barytes, starch, etc.

Graphite would be recognized by its blackness and lustre. It would be difficult to burn, requiring a high temperature or a stream of oxygen. Soap

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[1] *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 1178.

stone and *barytes* would not dissolve in dilute hydrochloric acid, and could be filtered off and identified by the usual qualitative tests. *Free lime* would give a red colour with phenolphthalein; *chalk* would not, but would effervesce on adding acid. *Starch* would be detected by the blue colour with iodine.

X.—DETERMINATION OF ASH.

The ash of any oil or fat free from water may be determined by weighing 10 grms. in a tared platinum dish, placing the dish at the mouth of a gas muffle heated to dull redness, and, as soon as the oil begins to smoke, igniting it with a match. The dish is then placed in such a position that the oil will burn quietly away, most of the smoke being drawn into the muffle (which is perforated at the back). When nothing but a charred mass remains, the dish is placed inside the muffle until the carbon is completely burnt off, then carefully removed to a desiccator to cool, and weighed. The particles of ash are often very light, and may easily be carried away by currents of air.

In 22 samples of pure mineral oil examined by Archbutt, mostly dark-coloured machinery oils for railway work, the percentages of ash were:—*maximum*, 0·055; *minimum*, 0·002; *average*, 0·015. In 36 samples of dark cylinder oil, the following percentages were found:—*maximum*, 0·080; *minimum*, 0·002; *average*, 0·025. These ashes were generally red in colour, and probably consisted largely of oxide of iron from the still. Pale, refined, mineral oils may be expected to leave much less ash than the majority of these samples. If a high ash be found in a pale mineral oil, an aluminium soap ('viscom,' 'gelatin') may have been added to produce a factitious viscosity; in that case the ash will consist, chiefly, of alumina.

Pure fatty oils and fats leave mere traces of ash, bone fat, which contains lime, being an exception.

Soap-thickened greases which contain water should first be heated over a very small flame and stirred with a platinum rod until all the water has evaporated. The dish, and the rod which should have been weighed with it, are then placed in the mouth of the muffle and treated as above directed. In the presence of soap, more or less considerable quantities of ash will be obtained, consisting of calcium or sodium carbonates, etc., etc., according to the nature of the soap.

Y.—DETECTION OF NITROBENZENE AND NITRO-NAPHTHALENE.

These compounds are used for the purpose of disguising the presence of mineral oils, by destroying their fluorescence or 'bloom.' Nitrobenzene is easily recognizable by its powerful and characteristic odour of oil of bitter almonds, but nitronaphthalene cannot be

detected by its smell. Greases are frequently scented with nitrobenzene to disguise the nature of the fat or oil used in their preparation. For the detection of nitronaphthalene, the following test, depending upon its reduction to naphthylamine, has been proposed by Leonard[1] and by Holde.[2]

A few cubic centimetres of the oil are warmed in an Erlenmeyer flask with zinc dust and dilute hydrochloric acid, and the mixture is frequently agitated. During this process, the fæcal odour characteristic of α-naphthylamine will be perceived. After the reduction is complete, the contents of the flask are poured into a separating funnel, and the acid liquid is drawn off through a filter paper into another separating funnel. It is there treated with sufficient caustic soda solution to redissolve the zinc hydrate at first precipitated, and, after cooling, is shaken with ether, which dissolves the liberated α-naphthylamine, the presence of which is indicated by the violet colour and fluorescence of the ethereal solution. The latter, after drawing off the aqueous liquid and washing with water, is evaporated to dryness, leaving a residue of the violet-coloured base. On treating this residue with a few drops of hydrochloric acid, the chloride is formed, which remains partly insoluble and partly soluble, but, on evaporating the excess of acid and adding water, a clear aqueous solution is obtained, in which ferric chloride gives an azure-blue precipitate. When filtered, this precipitate becomes purple-red, and the filtrate blue-violet. Instead of treating the residue with hydrochloric acid, and testing with ferric chloride, it may be dissolved in a little alcohol. On then adding a drop of a solution of sodium nitrite acidified with acetic acid, a yellow colour is produced, which is changed to crimson by hydrochloric acid.

Nitrobenzene, if present, is reduced by the zinc dust and hydrochloric acid to aniline, which is obtained on evaporating the ethereal solution as described above, either pure or mixed with α-naphthylamine, according to whether nitronaphthalene were simultaneously present or not. On treatment with hydrochloric acid, pure aniline dissolves readily, and on diluting and adding ferric chloride a green precipitate is produced, which afterwards turns deep blue, and does not become purple-red even on long standing; the filtrate, instead of being blue-violet, is yellow. When α-naphthylamine and aniline are present together, the precipitate is at first azure-blue, afterwards dirty red-brown, finally purple-red, and the filtrate is violet.

Z.—DETECTION AND DETERMINATION OF WATER.

The presence of water in pale oils is indicated by the appearance of turbidity, or by actual visible drops of water which sink in the oil, instead of rising as air-bubbles do. Water in greases is indicated by the frothing and crackling which occurs when a small quantity of the grease is heated in a dry test-tube, and by the condensation of drops of water on the upper, cool part of the tube; whilst the grease, if free from water, will melt quietly to a clear fluid. A more delicate test for the presence of traces of water in oils (especially dark oils) is recommended by Holde. A small quantity

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[1] *Chem. News*, lxviii. (1893), p. 297.
[2] *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 906.

(3 or 4 c.c.) of the oil is placed in a small dry test-tube, the interior of which is first coated all over with a film of the oil. The end of the tube containing the oil is then heated by being immersed just below the surface of a paraffin bath at 160°–180° C., when, if the sample contains water, the vapour will condense on the cool, oily, inner surface of the tube, above the level of the oil, forming a visible, cloudy emulsion.

The determination of water in lubricating greases may be made by one of the following methods :—

1. *By heating in an air-bath at* 105°–110° *C.*—About 5–10 grms. of the well-mixed grease are placed in a small tared beaker, and the exact weight is taken. The beaker is then heated in the air-bath at 105°–110° C. until frothing has ceased and the grease has melted down to a clear oil free from visible drops of water. It is then cooled and re-weighed.

2. *By stirring with a thermometer over a naked flame.*—100 grms. of the grease are heated in a weighed porcelain basin over a small flame, and continually stirred with a thermometer at a temperature not exceeding 105° C. (221° F.), until frothing has ceased and the grease is in calm fusion. The basin and contents, when cold, are reweighed. If the thermometer bulb be well drained into the basin whilst hot, the small quantity of adhering fat may be neglected ; or, the bulb may be wiped with a small piece of filter paper counterpoised with the basin.

CHAPTER VIII.

THE analytical examination of lubricants is conducted with different objects and on different lines according to the nature of the sample to be tested. If this be an undescribed oil, the primary object is to ascertain whether the substance is a hydrocarbon oil free from fixed oil, a fixed oil or fat free from hydrocarbon oil, or a mixture of the two. An undescribed hydrocarbon oil may be a mineral oil from petroleum or shale, a rosin oil, a coal-tar oil, or a mixture of these. A mineral oil is subjected, chiefly, to physical tests to ascertain its viscosity, flashing-point, etc., in order to determine whether it is suitable for use as a spindle oil, a machine or engine oil, or a cylinder oil ; and to such chemical tests, in addition, as will show whether the oil has been sufficiently refined, and is free from acidity and from rosin and coal-tar oils. A fixed oil, such as rape oil, olive oil or tallow, is tested first of all to ascertain whether it is sufficiently free from acidity (see p. 218), and then more elaborately to prove whether the sample is genuine or adulterated, and especially whether any oil of drying or semi-drying character has been added which would tend to increase the natural tendency of the oil to thicken or gum by oxidation. A mixed lubricant (which includes most greases) containing both hydrocarbon oil and fixed oil, in addition perhaps to soap, water, etc., is first tested qualitatively to find out the nature of the main ingredients, and then a more or less complete quantitative analysis is made with the object of ascertaining the composition of the mixture. The information thus obtained may be supplemented by viscosity and other tests, as in the case of a pure mineral oil.

A.—UNDESCRIBED OILS.

The nature of an undescribed lubricating oil, if simple and not a mixture, is almost always indicated by the smell, taste, or appearance (colour, fluorescence, consistency, etc.). How much can be determined in this way in the case of a mixed oil depends upon the experience

of the observer. The smell is best observed by pouring a little of the oil into the palm of the hand, rubbing it with the fingers, and smelling the warm oil. Sometimes the oil may with advantage be heated in a capsule or small basin.

The specific gravity of the oil may next be taken, by the bottle method (p. 173) if the oil be a thick fluid, or by the Westphal balance (p. 175) if it be a thin fluid. Reference to the following table will then show to which class the oil, if pure of its kind, can belong :—

<center>SPECIFIC GRAVITIES AT 60° F.</center>

Vegetable and animal oils,	0·879–0·968 [1]
Mineral oils from petroleum and shale,	0·860–0·990 [2]
Rosin oils,	0·960–1·01
Heavy coal-tar oil (grease oil),	1·065–1·100 (*Hurst*)

A pure rosin or coal-tar oil will be recognized by the smell and high specific gravity of the sample, and it will only remain to apply confirmatory tests, such as the acetone test (p. 295) and the Liebermann-Storch test (p. 293) to identify rosin oil. The very characteristic smell and high specific gravity of coal-tar oil is sufficient to identify it without further test.

The probability is, however, that the sample will turn out to be either a mineral oil, a fixed oil, or a mixture of the two, and to distinguish between them in a preliminary way the tests described in Chapter VII, section B. (p. 219) may be applied. The further investigation will be then found in one of the following sections.

<center>B.—MINERAL OILS.</center>

By large consumers, mineral lubricating oils are usually purchased to specifications describing the character of oil which has been found by practical experience to be the most suitable for the purpose required, and the object of the examination is, therefore, to ascertain whether the sample possesses the specified characters. Such specifications should state whether a natural, reduced, or refined oil is required, what the viscosity, specific gravity, flashing-point, and setting-point must be, and the degree of purity necessary.

Colour, Appearance, and Odour.—Whether an oil is a natural, reduced, or refined oil is ascertained mainly by its appearance, but also to some extent by other tests. Natural and reduced oils are usually · dark in colour and opaque, brownish or greenish by reflected light, and often fluorescent   Refined oils vary in colour from pale amber to orange or deep red, are generally fluorescent, and

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[1]·Vegetable fats (Japan wax, palm nut oil) have a higher sp. gr. (see Table XLII., p. 184).

[2] The sp. gr. of mineral lubricating oils rarely exceeds 0·947.

are either perfectly bright and transparent (spindle oils and some engine oils) or merely translucent (charcoal-filtered cylinder oils).

For the sake of uniformity, the colour and appearance should be observed under standard conditions, *e.g.* in a ¼-inch (Lovibond) glass cell with parallel flat sides, held first between the eye and a window (appearance by transmitted light), and then with the observer's back to the window (appearance by reflected light). Fluorescence may be observed by looking down into the cell, held below the edge of a table or bench fronting a window. Redwood examines pale-coloured oils by means of Lovibond's tintometer, using a 2-inch cell and matching the colour by means of coloured glasses.[1]

Mineral lubricating oils should not have any empyreumatic odour.

Viscosity.—This is the most important property of a mineral oil which can be measured in the laboratory. The knowledge of it determines whether an oil is suitable for use as a spindle oil, an axle oil, a machine or engine oil, or a cylinder oil. The determination is usually made at two temperatures, viz. at 60° or 70° F. if the oil be fluid at those temperatures, and, in the case of spindle and machine oils, also at 100° or 140° F. In order to ascertain the extent to which the viscosity is affected by rise of temperature, cylinder oils are conveniently tested at 100° and 212° F; there is not much to be gained by making tests at higher temperatures, though in Redwood's viscometer a determination can be made at as high a temperature as 400° F. The determination should be made either by Redwood's viscometer (p. 144) or by Coleman's (p. 147); the latter is most convenient for temperatures up to 212° F. All results should be expressed, if possible, in absolute measure (p. 155) as well as in terms of rape or other known oil. The viscosities of a number of oils, in dynes per sq. cm., are given in the table on p. 167.

Specific Gravity.—This is determined by one of the methods described in Chapter VI., section B (p. 172), and little need be added to what has there been said. The bottle method is most suitable for the thicker oils, but the Westphal balance may be used for spindle oils and the lighter machine oils. The specific gravity is of secondary importance in regard to the lubricating value of an oil, but it serves to identify the particular oil required, and in some measure to detect the presence of rosin and tar oils. Where there is a choice between two or more oils from a given source, all having the required viscosity, preference should be given to those of lowest specific gravity. The specific gravities of mineral lubricating oils are given in the table on p. 185.

Flashing-point and Volatility.—The flashing-point, determined by the Pensky or Gray testers (pp. 188, 190), should not be lower than 300° F. for outdoor machinery and 340° F. for mill work. Cylinder oils should flash at temperatures well above that of the cylinder in which they are intended to be used, say at from 450° F. to 600° F. All cylinder oils should be tested for volatility by the method described

on p. 191, and should not lose more than 1 per cent. in one hour at the temperature of the steam from the boiler.

Machine oils may also with advantage be submitted to this test, and the loss of weight in one hour at, say, 370° F. determined. A great difference will be found in this respect between oils obtained from different crude petroleums. The results given in the following table illustrate this; the four oils, numbered 1 to 4, being all American mineral engine oils of the red type.

TABLE LXXXIX.—VOLATILITY TESTS OF MACHINE OILS.

	1.	2.	3.	4.
Viscosity (absolute), at 60° F.,	2·13	2·99	2·51	5·48
Viscosity (absolute) at 100° F.,	0·56	0·61	0·61	0·97
Flashing-point (closed test), .	372° F.	358° F.	356° F.	346° F.
Loss of weight in 1 hour at 370° F.,	9·1 %	45·2 %	18·9 %	26·7 %

It will be noticed that the oils differ very much as regards volatility at 370° F., and that the volatility has no relation to the viscosity and very little relation to the flashing-points of the oils.

Machine oils flashing below 300° F. should be tested for volatility at 100° F. and 200° F., the test being continued until the oil ceases to lose more than 0·5 per cent. in one hour. A good lubricating oil should lose little or nothing at these temperatures. A 'natural' mineral oil flashing at 200°–210° F. was found to lose 6 per cent. by evaporation at 100° F. and 17 per cent. at 200° F.

Setting-Point or Cold Test.—This, in the case of oils (not greases), should obviously be as far as possible below the temperature at which the oil is to be used. The test is, of course, most important in the case of oils for outdoor machinery, such as railroad oils. For such purposes, summer oil should remain fluid at 32° F., and winter oil at 15° F., if possible; but allowance must be made for American oils, which will not, as a rule, withstand so low a test. (See table on p. 200.)

General Purity and Freedom from Adulteration.—In addition to the foregoing, there are certain tests as to which circumstances must decide whether they should be made or not; these are for the detection of impurities, unacknowledged additions, or adulterants. The chief of such substances to be looked for in mineral oils are:

(a) *Soap.*—Every mineral oil which has a non-homogeneous appearance, or an unnatural viscosity, or which exhibits a tendency to form threads in dropping, should be tested for soap by the methods described in Chapter VII., section W (p. 303). If soap be found, its

nature can be ascertained by the analysis of the ash (see p. 304; also section E, p. 224). By well shaking some of the soap-thickened oil with dilute hydrochloric acid in a stoppered bottle heated by immersion in hot water, then pouring the contents into a separating funnel, drawing off the acid, and well washing the oil with hot water, the mineral oil can be obtained in its natural state and its true viscosity determined.

(b) *Ash.*—Every mineral oil leaves some ash when burnt, but the quantity is usually minute (see p. 304). In an oil the origin of which is unknown, the amount of ash should always be determined. An abnormally high ash indicates either the presence of soap or imperfect refining.

(c) *Fixed Oil or Fat.*—An oil sold as a pure mineral oil and at a low price is not likely to contain a fixed oil; but special brands of mineral oil, especially cylinder oil, not unfrequently do contain an unacknowledged small quantity of animal or vegetable oil to which some good or bad quality, revealed in practice, may be due. Therefore, in testing an unknown oil alleged to be purely mineral, it is always desirable, sometimes most necessary, to prove the absence of fat by careful chemical analysis. For this purpose Ruhemann's test may be used (p. 219), but the quantitative method described on p. 235 is the only absolutely certain test.

(d) *Acidity.*—Any refined mineral oil containing more than 0·2 per cent. of total acidity, calculated as oleic acid, should be tested for free mineral acid (usually sulphuric). The method is described on p. 217. It is seldom necessary to test natural and reduced oils. Abnormally high acidity may, of course, be due to the presence of rosin acids contained in rosin oil added as an adulterant; therefore, time might be saved by testing for rosin oil before testing for mineral acid. Rosin acids can, if desired, be isolated by the method described on p. 238.

(e) *Rosin Oil.*—The methods of detecting and determining the proportion of this adulterant are described at pp. 293–295.

(f) *Gumming Property.*—This is scarcely a property of pure mineral oils, as such oils do not gum like the fixed oils. The remarks under this head on pp. 272–278 should be read, where the causes which may lead to the formation of deposits by mineral oils are discussed. If there be any reason for investigating the tendency to form a gummy or sticky residue which a pure mineral oil may appear to exhibit in practice, the 'film test' described on p. 266 may be used. In some cases it may be desirable to make such a test upon a surface of steel or other metal, or upon a painted surface.

(g) *Asphalt and Tar.*—Little need be added to what has been said in Chapter VII., section U (p. 300), except that the special tests for these bodies are seldom necessary in the case of Russian and American oils, and need only be made if the practical results indicate their presence in an objectionable degree.

(h) *Caoutchouc.*—According to the authors' experience, this is a

rare aduíixture. If, however, stickiness or unnatural viscosity of a mineral oil be found, notwithstanding the absence of soap, then caoutchouc should be searched for. See p. 302.

(*i*) *Mechanical Impurities.*—Grit and dirt in a mineral oil would be detected by straining the oil through fine wire gauze or muslin. Water is detected by the tests described in section Z (p. 305).

C.—FIXED OILS AND FATS.

The most important and useful physical and chemical data for the recognition of the lubricating oils belonging to this class are included in the table on pp. 314-315, and in the following pages hints for the examination of each oil are given.

The first test to make in examining any fixed oil intended for lubrication is the determination of *acidity*. This is especially important in the case of olive oil, tallow, palm oil, and coconut oil. The two last, as commercially met with, are usually quite unfit for lubrication. The more delicate and intricate the machinery, the greater the need for selecting the least acid oil, and the smaller the maximum amount of acidity permissible; for no machinery should oil be used containing more than 4 per cent. of free (oleïc) acid. The reason for this statement and the methods of determining acidity will be found in Chapter VII., section A (p. 210).

Wool or cloth oils are not here alluded to. They often contain very large amounts of free fatty acids; indeed, commercial oleic acid is used as a wool oil under the name of 'oleine'; such oils are quite. unsuitable for the lubrication of machinery.

Rape Oil.

Refined rape oil for lubrication and burning should be clear, and pale yellow in colour.

The **total acidity,** calculated as oleic acid, should not exceed 3 per cent. Of 378 samples of commercial refined rape oil examined since 1901, 91 per cent. satisfied this condition (see p. 211). Low acidity is of great importance if the oil be required for burning in lamps, since free fatty acids, as well as free mineral acid, have a charring action upon the wick.

. In rape oil refined by sulphuric acid, traces of free sulphuric acid exist, as is proved by the following experiments.

100 c.c. of rape oil and 100 c.c. of distilled water were placed in a large beaker on a steam-bath, and steam was blown through .the mixture vigorously for half an hour. The oil and water were then poured into a separating funnel, the water was drawn off through a filter-paper, and the oil was washed with a little more water. ...trating the aqueous liquid to rather less than 50 c.c., it ...d. and the filtrate was titrated with decinormal

soda, using methyl orange as indicator. The following results were obtained : —

Oil Refined at								Sulphuric Acid (H_2SO_4) per cent.
Stettin,	.	.	.	.	.	.	.	0·0056
Hull, 1st sample,	.	.	.	.	.	.	.	0·0050
Hull, 2nd sample,	.	.	.	.	.	.	.	0·0026

The neutralized liquids were boiled down to 2–3 c.c. and tested with barium chloride, and in each case a precipitate of barium sulphate was obtained, which was estimated by the eye to about correspond with the result obtained by titration. These samples being commercial oils of good quality, not selected, it may be assumed that the percentage of *free mineral acid* in refined rape oil should not exceed 0·006 per cent. of H_2SO_4, which is equivalent to 0·035 per cent. of oleic acid.

The **specific gravity** of genuine refined rape oil suitable for lubrication usually lies between 0·914 and 0·9155 at 60° F. ; it should not exceed 0·9160, and if above 0·9165 either ravison or other oil of more strongly drying character than rape is probably present. A lower sp. gr. than 0·914 would be suspicious, for, although perfectly genuine rape oil may be as low as 0·9132 in sp. gr., such oil is seldom met with in this country. An abnormally low sp. gr. might be due to adulteration with light mineral oil.

The **viscosity** of rape oil is exceptionally high, and is a very valuable indication of its purity. All fixed oils, except castor oil, likely to be added as adulterants would lower the viscosity, and although this could be counteracted by adding castor oil or blown oil, the presence of these oils would be indicated by other abnormal characters, castor oil raising the acetyl value and both oils raising the specific gravity. Rosin oil or heavy mineral oil, if present, would be detected in the unsaponifiable matter.

The **saponification value** of genuine rape oil ranges from 17·00 to 17·50 per cent. A value in excess of 17·50 would indicate the presence of ravison or other more strongly drying oil. On the other hand, a value lower than 17·0 would indicate the presence of an unsaponifiable oil, or, possibly, of sperm or Arctic sperm oil. The test must, of course, be made with every precaution to ensure accuracy, otherwise the limits cannot be so strictly defined.

The **Maumené value**, or rise of temperature on mixing 50 grms. of the oil with 10 c.c. of sulphuric acid (containing 97 per cent. H_2SO_4), ranges from about 58° C. to 64° C. ; the result depends to some extent upon the 'personal equation' of the operator, which is not serious if the instructions given on p. 262 are strictly adhered to. A high result indicates the presence of ravison or other drying or semi-drying oil, and a low result indicates mineral or sperm oil.

The **unsaponifiable matter**, determined by the method on p. 225, should not exceed 2 per cent. in genuine commercial rape oil. In the expressed oil it is usually below 1 per cent., but in the oil extracted

TABLE XC.—VEGETABLE AND ANIMAL

Reference to complete Tables page	Physical and Chemical Constants.	Rape Oil. (Colza Oil.)	Olive Oil.	Castor Oil.	Palm Oil.
184	Specific gravity at 60° F.,	0·914–0·916	0·914–0·917	0·959–0·968	0·921–0·925
167	Viscosity (dynes per sq. cm.),	1·09–1·16 at 60° F.	1·00 at 60° F.	2·73 at 100° F.	..
199	Solidifying-point, °F.	11–28	21–39	−0·4 to +14	
204	Melting-point, °F.	..	..	..	80–97 when free from excess of acid
207	Oleo-refractometer value at 22° C.,	+15° to +20°	0 to +3·5°	+37 to +46°	..
222	Saponification value,	170–17 5	18 5–19·6	17·6–18·7	19·6–20·6
230	Hehner value,	95·0–95·1	94–96	95 3–95 5	94·2–97
242	Reichert value ; c.c. per 2·5 grms.,	0·0–0·8	0·3	1·4	0·5–0·8
242	Reichert-Meissl value ; c.c. per 5 grms ,	0·0–0·3	0·45–1·5	1·1–4·0	0 7–1 0
250	True acetyl value (Lewkowitsch),	1·47	1·06	14·67–15·05	1·60
255	Iodine value,	94·1–105·6	76·2 91·7 (usually 82–87)	81·4–90·6	53 57·4
263	Maumené thermal value ; 50 grms. oil, 10 c.c. of 97 % sulphuric acid, °C.,	58–64	40–45	56–66	..
233	Unsaponifiable matter, %,	0·6–1·5	0·8 1·5	0·3–0·8	1·25
	Mixed Fatty Acids.				
185	Specific gravity at $\frac{100°}{100°}$ C.,	0·875–0·876	0·874–0·876	..	0·870
205	Solidifying-point or titre-test, °C.,	12·2–18·5	17·2–26·4		35·9–45·5
205	Melting-point, °C.,	16–21	19 28·5	13	41–50
255	Iodine value, %,	96·5–105·6	86–90·2	86·5–88·5	53·5
	Mixed Alcohols.				
185	Specific Gravity at $\frac{100°}{100°}$ C.,	..		..	
201	Melting-point, °C.,			..	
255	Iodine value, %,	..		..	
214	Saponification value of Mixed Acetates, %,	..	..	..	

OILS USED FOR LUBRICATION.

Tallow (Beef and Mutton).	Tallow Oil. (Ox Oil.) (Animal Oil.)	Lard Oil.	Neatsfoot Oil.	Sperm Oils.		Porpoise and Blackfish Jaw Oils.	Ben Oil.	Hazel-nut Oil.
				Southern.	Arctic.			
0·937-0·953	0·916-0·919	0·913-0·919	0·914-0·919	0·875-0·884	0·879-0·881	..	0·91?-0·920	0·916-0·917
0·18 at 150° F.	1·04-1·13 at 60° F.	0·99 at 60° F.	about same as tallow oil	0·39 0·42 at 50° F.		.	..	..
..	variable, say 32-46	25-42 (occasionally lower)	..	about 32		..	32-48	-4 to +14
108-124	..	..	..	..		..	..	..
..	..	0' to +1'	-1° to -4	-12' to -17'		..	..	..
19·0-19·8	19·3-20·0	19·1-19·6	19·4-19·9	12·0-14·7	12·3-13·6	25·4-29·0	18·5-18·8	18·7-19·7
95-96	..	..	95·3-95·5	..	..	66·3-72·1	..	95·5
..	0·25	..	..	1·3	1·4	47·8-65·9	..	..
1·0-1·2	1·0 1·2	.	..	.	..	131·6	..	0·09
0·24-0·86	1·85	0·26	0·22	0·45-0·64	0·41-0·64	..	..	..
33·7-49·3	55-60	67-88 (according to setting point)	66·8-72·9	81·3-90·1	67·1-84·6	31 50	72-113	83-90
..	40-43	41-46	(40 46·)	45-51	42-47	.	..	..
0·5	..	..	.	37·4 41·5	31 7(?)-39·7	..	..	..
0·870	..	..	0·874-0·880	..	..	..	..	..
33·5-48·3	..	..	26 27 (sheep's foot oil 21-22; horse's foot oil 28·6)	11·1-11·9	8·3-8·6	.	37·2-37·8	..
49-54	..	..	..	13·3	10·3-10·8	..	..	17-25
95-96·3	..	..	..	83·2-88·1	82·2-83·3	..	..	90·1-90·6
..	..	..	..	0·8271	..	..	..	..
..	..	..	..	23·5-27·5	..	..	..	..
..	..	..	..	50·5-60·3		..	..	..
..	..	..	18·49		18·62	..	..	..

from the seed by petroleum spirit 1 per cent. must be allowed for residual hydrocarbons. If a larger proportion than 2 per cent. be obtained, it should be purified by resaponification as directed on p. 234, and if still materially in excess of 2 per cent., the product should be examined as directed in Chapter VII., section F (p. 228), to ascertain whether hydrocarbons (mineral or rosin oil), cholesterol (from animal oils), or wax alcohols (from sperm or bottlenose oils) are present. In genuine rape oil the unsaponifiable matter consists very largely of phytosterol, which may be obtained in characteristic tufts of needle-shaped crystals by dissolving the unsaponifiable matter in 2–3 c.c. of warm 90 per cent. alcohol and cooling the solution.

Rape oil should always be subjected to the **oxidation test** described on p. 265 (watch-glass test), a standard sample of known purity being tested at the same time and under the same conditions.

Halphen's **colour reaction** for cottonseed oil (p. 288) and the furfurol test for sesamé oil (p. 291) should not be omitted ; both are very delicate, and the result must be interpreted in accordance with the quantitative values. These reactions may be relied upon to give negative results with genuine rape oil. If a red colour be obtained by Halphen's test, the presence of cottonseed oil may be confirmed by the Milliau test (p. 289), using the fatty acids, which can easily be obtained from the soap solution left after isolating the unsaponifiable matter. Some genuine rape oils have a slight, slow reducing action on the silver solution ; but an immediate, decided reduction proves the presence of cottonseed oil, and the amount of reduction is usually in proportion to the percentage of cottonseed oil present.

The above named tests suffice for the detection of the usual adulterants, viz. :—*ravison, cottonseed, maize, linseed and the drying oils, fish oils, mineral oil,* and *Arctic sperm oil.* The latter, though usually more expensive than rape oil, is sometimes added in order to adjust the specific gravity and saponification values which have been raised by adulteration with oil such as cottonseed.

As a supplementary test, the **iodine value** is useful for confirming the presence of ravison oil, maize oil, the drying oils, and some fish oils, which have higher iodine values than genuine rape oil. It is of no use for the detection of cottonseed oil. These oils (except cottonseed) lower the solidifying and melting-points of the mixed fatty acids. Thus, the fatty acids of genuine rape oil solidify at $10 \cdot 5°$ to $18 \cdot 5°$ C., but the acids from ravison oil do not solidify at $0°$ C.

Olive Oil.

Pure neutral olive oil is one of the best lubricants we possess, but unfortunately a great deal of it is spoiled previous to extraction, by allowing the pulp to ferment and the oil to become decomposed (see pp. 112 and 211) ; also by storing the oil in a crude state. Olive oil intended for lubrication must therefore be carefully examined for acidity (p. 216). 4 per cent. of free oleic acid should be the maximum

allowed by large consumers; small quantities of oil intended for the lubrication of delicate machinery should be purified from every trace of acid by refining with soda (see p. 218).

Olive oil should be clear, and pure yellow or greenish-yellow in colour. Some genuine olive oils are green or brownish-green, the colour being due to chlorophyll, which may be identified by means of its characteristic absorption bands if the oil be submitted to spectro-scopic examination. But there are some adulterated oils which are artificially coloured green by *copper* ; this may be detected by diluting some of the oil with ether and shaking with dilute sulphuric acid, which will remove the green colour. On drawing off the acid liquid and adding excess of ammonia, the deep blue colour characteristic of cuprammonium will be obtained.

Olive oil, being one of the most expensive lubricating oils, is very liable to adulteration. The most valuable instrument for the rapid detection of adulteration is the **oleo-refractometer** (see p. 208). As will be seen by reference to the table on p. 207, the recorded deviation caused by genuine olive oil ranges from $0°$ to $+3·5°$. 106 samples examined by Oliveri[1] ranged from $0°$ to only $1·2°$. All fixed oils likely to be added as adulterants would increase the refraction, except lard, neatsfoot, and tallow oils. Arachis oil, which has a deviation of only $+3·5°$ to $+7·0°$, would not be detected, unless present in large proportion, but would be found by **Renard's test** (p. 283).

The **specific gravity** of fairly neutral olive oil at 60° F. usually ranges from 0·915 (rarely 0·914) to 0·917, but may, it is said, rise to 0·919 in the case of dark-coloured samples containing the oil from the kernel and endocarp.[2] Such oils should not be used for lubricating without a very careful examination as to their tendency to oxidize and gum, 0·5 grm. of the oil being exposed to the air at 212° F. on a watch-glass for sixteen hours side by side with the same weight of a sample of known good quality. All olive oils over 0·917 in specific gravity should be subjected to this test and to a very complete examination for adulterants, such as cottonseed, sesamé, curcas, and poppyseed oils. Adulteration with rape or earthnut oil would not be indicated by the specific gravity.

The (*Wijs*) **iodine value** of genuine olive oil usually ranges from 82·0 to 87·0 ; averaging about 84·5. Some oils are met with having a lower value, even as low as 76·2. This was the (*Hübl*) iodine value of an olive oil examined by one of the authors, which was found to possess a quite normal specific gravity (0·9157 at 60° F.), saponifica-tion value (19·03 per cent.), and viscosity ; the unsaponifiable matter amounted to only 0·88 per cent., arachis oil was absent, and the colour reactions for cottonseed and sesamé oils were quite negative. The acidity was 3·5 per cent. The low iodine value appeared to be

[1] *Jour. Soc. Chem. Ind.*, xiii. (1894), p. 45.

[2] Genuine Tunisian olive oil, it is said, may have a specific gravity of 0·919 at 15° C. and an iodine value as high as 89·4. See *Chemical Trade Journal*, vol. xxviii. (1901), pp. 388, 504, and 524.

due to an excess of palmitin, the oil being unusually sensitive to cold
and depositing a large proportion of solid fat at a temperature of 46°
to 47° F. A few olive oils of this kind have been met with, all of
which had an iodine value below 80·0 per cent.[1] Thomson and
Dunlop in a recent paper record *Wijs'* values of 82·2 to 89·1, obtained
with olive oils prepared by themselves from the fruit and, therefore,
undoubtedly genuine.[2] Higher numbers still have been recorded for
Dalmatian and Tunisian oils.[3] It is said that, in California, olive oil
is adulterated extensively with mustard oil from the white mustard
(*Brassica (sinapis) Alba*) which grows there in great profusion.[4]
This oil would raise the iodine value, and would at the same time
lower the saponification value. Mustard oil contains arachidic acid,
which would be a further means of detection.

The **saponification value** of genuine olive oil, according to De
Negri and Fabris, who examined 203 samples, may range from 18·5
to 19·6 per cent., and is usually 19·0. Of 400 samples of commercial
olive oil examined by one of the authors, the values ranged from
18·80 to 19·29 per cent. A low saponification value might be due
to the presence of olive-kernel oil (which can scarcely be regarded as
an adulterant), or to adulteration with rape, mustard, sperm, or
mineral oil. No adulterant likely to be added would materially
raise the saponification value of olive oil.

The **Maumené value** of genuine olive oil, determined as directed
on p. 262, is lower than that of any other vegetable oil, ranging,
according to our experience, from 40° to 45° C.; this test is, therefore,
of great value for the detection of adulteration.

The **unsaponifiable matter** in genuine olive oil does not exceed
1·5 per cent.; a higher result than this would probably be due to the
presence of hydrocarbon (mineral or rosin) oil, or of wax alcohols
from Arctic sperm oil.

With reference to specific adulterants, the following remarks may be
made :—

Cottonseed oil, unless it has been heated, would be detected with certainty
by Halphen's test (p. 288) or by the Milliau test (p. 289), both of which
give negative results with pure olive oil and are sufficiently delicate to
detect as little as 2 per cent. of cottonseed oil, if present. Olive oil adulter-
ated with cottonseed oil would, of course, contain more than this percentage,
and the presence of the foreign oil would be confirmed by the increased
refractive power, iodine value, and Maumené value of the sample, also by the
result of the oxidation test ; without this confirmation of the colour reactions,
the presence of cottonseed oil as an adulterant could not be certified.

Sesamé oil would be detected, with certainty, by the very delicate
Baudouin reaction (p. 291). Some genuine olive oils give a pale rose-red
coloration, but it is unlikely for error to occur if the sample be submitted to
confirmatory quantitative tests. Sesamé oil, if present as an adulterant in

[1] Lard oil was not looked for in these samples.
[2] *Analyst,* 1906, p. 281.
[3] Lewkowitsch, *Analysis of Oils, etc.*, p. 627. See also note 2 on p. 317.
[4] Brannt; *Treatise on Oils,* vol. 1. p. 487.

olive oil, would raise the refractive power, iodine value, and Maumené value of the oil, and would increase its drying and gumming property.

Earthnut (Arachis) oil can only be detected in olive oil by Renard's process, although the presence of the oil might possibly be indicated by an abnormally high iodine value. Earthnut oil of the best quality is a non-drying oil, and if a sample of olive oil containing this oil be found to possess no undue tendency to oxidize, there is only the substitution of a cheap oil for one of greater value to be objected to. Some earthnut oils are not 'non-drying,' and olive oil containing such is spoiled for lubrication. It must not be forgotten that rape, mustard, and perhaps other oils from cruciferous plants contain arachidic acid. These oils would betray their presence by lowering the saponification value, and by raising the iodine and Maumené values, of olive oil.

Castor oil would raise the specific gravity, viscosity, and acetyl value of the sample, besides increasing the solubility of the oil in alcohol.

Curcas oil would raise the specific gravity and the Maumené and iodine values, and would increase the tendency to oxidize.

Arctic sperm oil, also *mineral* and *rosin oils*, would betray their presence by increasing the percentage of unsaponifiable matter, and could be identified with certainty and the amount determined by examining the latter.

Lard and *tallow oils* would be the most difficult to detect. They would probably raise the freezing-point ; but, being non-drying oils and good lubricants, their presence would not necessarily be objectionable, except for the fraud. The best method of detecting the presence of either of these oils in olive oil would be to isolate the stearin, which is absent from pure olive oil (Hehner and Mitchell, *Analyst*, xxi. (1896), p. 316), or to apply the phytosterol acetate test (see p. 232). The phytosterol isolated from pure olive oil melts at 135°–136·5° C. ; its acetate melts at 120·3°–120·7° C. (Gill and Tufts).

Castor Oil.

Castor oil for lubricating should be clear, pale in colour, and as free as possible from acidity.

For the detection of adulterants, advantage may be taken of the easy **solubility** of genuine castor oil **in alcohol**. Absolute alcohol dissolves castor oil in every proportion ; 90 per cent. alcohol (sp. gr. 0·834) dissolves less, 1 volume of castor oil requiring from 2·4 to 2·94 volumes of 90 per cent. alcohol at 20° C. according to experiments by Itallie.[1] A sample of genuine castor oil tested by Archbutt was perfectly soluble in 2 volumes of 90 per cent. alcohol at 15° C. Twenty-three samples of Indian castor oil, examined by Deering and Redwood, were completely soluble in 3 volumes of alcohol of sp. gr. 0·830 at 60° F. (15·5° C.). It appears, therefore, that castor oil, if genuine, should dissolve completely in 3 volumes of 90 per cent. alcohol at 20° C. It is usual, however, to employ 5 volumes of alcohol, as recommended in the *British Pharmacopœia* (1898), and we have found by experiment, with the sample of easily soluble castor oil referred to above, that when only 5 per cent. of either rape, blown rape, cottonseed, poppy, maize, or curcas oils were mixed with it, 5 volumes of 90 per cent. alcohol gave a strongly turbid mixture at 15° C., which deposited a small quantity of oil on standing. The

[1] Lewkowitsch, *Analysis of Oils, etc.*, p. 421.

following test, originally recommended by Finkener[1] (who used a slightly stronger alcohol), may therefore be employed with confidence as a rapid method of assay :—Measure exactly 10 c.c. of castor oil in a graduated, stoppered test cylinder, add 50 c.c. of alcohol (sp. gr. 0·834) and well mix. If genuine, a clear and bright solution will be obtained at 15° C. If as little as 5 per cent. of foreign oil be present, the liquid will remain strongly turbid even on warming to 20° C.

The **specific gravity** of castor oil should lie between 0·959 and 0·968, and is usually about 0·963–0·964. Adulteration with any other natural fixed oil or mixture of oils would lower the sp. gr., and although this might be adjusted by the addition of rosin oil (sp. gr. 0·96–1·01), the presence of the latter would be easily detected by determining the amount and examining the properties of the unsaponifiable matter, which, in genuine castor oil, does not exceed 1·0 per cent. Blown rape or blown cottonseed oil might be added without altering the density, and without causing any appreciable increase of the unsaponifiable matter.

The **viscosity** of castor oil greatly exceeds that of any other natural fixed oil, but it is exceeded by that of blown oil. Twenty-three samples of Indian castor oil, tested by Deering and Redwood in the Redwood viscometer, required from 1160 to 1190 seconds for the outflow of 50 c.c. at 100° F.

The **acetyl value** of castor oil (14·6 to 15·1 per cent.) exceeds that of any other known oil except grape seed oil (pp. 248, 250), and is one of the most valuable indications of its purity. Although blown oils also have a high acetyl value, they do not nearly approach castor oil in this respect (see p. 248), and the detection of 10 per cent. of blown oil in castor oil is possible. Grape seed oil, if present in castor oil, would lower the specific gravity.

The **Hehner value** (95·3 to 95·5 per cent.) would be lowered by adulteration with blown oil, as would also the iodine value (81·4 to 90·6 per cent.) ; on the other hand, the **Reichert-Meissl value** (1·1 to 4·0), the **Maumené thermal value** (56° to 66°), and the **saponification value** (17·6 to 18·7 per cent), would be raised.

Among other possible adulterants mentioned by Allen, *poppyseed oil* would lower the specific gravity, acetyl value, and viscosity, and would raise the iodine value ; *lard oil* would lower the specific gravity, viscosity, acetyl and iodine values ; *coconut oil* would lower the specific gravity and the Hehner and iodine values, and would raise the saponification value ; and *seal oil* would lower the specific gravity, acetyl value, and viscosity, and would raise the iodine value. *Cottonseed* and *sesamé oils* would be detected by the characteristic colour tests for these oils.

Palm Oil.

Palm oil is not, as a rule, adulterated with other fats, the chief impurities being free palmitic acid, dirt, and water. For grease-

[1] *Jour. Soc. Chem. Ind.*, vi. (1887), p. 148.

making, low acidity is of chief importance, as the dirt is strained off and the water settles out in melting.   The **acidity** is determined by the method described on p. 216, and should be neutralized by adding the necessary additional amount of soda in making the grease.   The proportion of **dirt** and **water** can be determined, roughly, by melting the sample in a 100 c.c. cylinder standing in a beaker of hot water, and reading off the volume of sediment which is deposited.   Anything under 2 per cent. may be neglected.   If over 2 per cent., an allowance is usually made by the seller.   In that case, a more accurate determination may be made by dissolving a weighed quantity of the well-mixed sample in ether, filtering, washing, evaporating the ether, drying the fat and weighing it; the difference between the weight of dry fat and the weight of the sample taken is water and dirt.

Palmnut and Coconut Oils.

The high **saponification** and **Reichert values**, and the low **iodine values**, of these two oils are characteristic, and afford ready means of distinguishing them from other oils and fats.

Coconut oil is said not to be adulterated.   If required for lubrication, the most important test would be the determination of **acidity**.

Tallow.

Tallow intended for lubrication, when melted in a test-tube, should be clear, and free from more than traces of suspended matter.   **Water**, if present, can be determined as directed on p. 306.   **Suspended impurities** (membrane, etc.) can be determined by dissolving a fair sample (10 to 20 grms.) of the tallow in ether or petroleum spirit, filtering through a weighed filter paper, washing out all fat with the hot solvent, and re-weighing the paper and contents.   The latter, if sufficient in amount, may then be examined for possible adulterants such as **starch, lime-soap**, etc.   In genuine tallow, the percentage of insoluble matter rarely exceeds 0·2, and of water 1 to 1·5.   (*Allen.*)

The **acidity** should, of course, be as low as possible, and should not in any case exceed 4 per cent. of oleic acid.   This would exclude such adulterants as distilled grease stearin and rosin.

The **saponification value** may range from 19·0 to 19·8 per cent., and averages about 19·44.   Paraffin wax (saponification value, nil) would lower the value; palmnut and coconut oils (sap. value 24·6 to 26·8) would raise it; bone-fat, cottonseed stearin, and cottonseed oil are without effect upon this constant.

The (*Hübl*) **iodine value** of genuine tallow has been found to range from 34·8 (*Thoerner*, 32·7) to 47·5, according to published figures. We have met with apparently genuine tallow absorbing as much as 49·3 per cent. of iodine; possibly, but improbably, bone-fat or horse-fat might have been present, but not cottonseed stearin or oil.   The

average iodine value is about 40, according to Alder Wright, 43 according to Archbutt; Rowland Williams puts it at 40 to 41, Lewkowitsch at 36 to 40. The range is about the same both for beef and mutton tallow, but the average is probably lower for the latter. Any tallow having an iodine value above 47·0 would be suspicious, and might contain cottonseed stearin (88·5 to 104), cotton-seed oil (100·9 to 116·9), horse fat (71·4 to 86·3), or bone fat (46·3 to 55·8). On the other hand, an abnormally low value, say below 38, might be due to the presence of paraffin wax (4·0), palmnut oil (10 to 17·5), or coconut oil (8·3 to 10·0). It is obvious that a mixture of the above fats and oils in suitable proportions might be made which would have the same iodine value as genuine tallow.

Cottonseed stearin and cottonseed oil, which are the most frequent adulterants of tallow, can, if present, be detected by the Halphen and Millian **colour reactions** (unless they have been previously treated so as not to give these reactions). Pure fresh tallow gives entirely negative results. (Note, however, Bevan's and others' observations with lard, p. 289.) The nitric acid colour test (p. 290) would still be available, but the results must be interpreted with caution. Allen states that tallow which has not been washed and purified, and which, therefore, contains particles of blood, acquires a light brown colour when agitated in a melted state with nitric acid of 1·38 sp. gr.

To prove the presence of cottonseed oil or stearin, L. Mayer recommends an examination of the 'oleine' obtained by allowing the melted tallow to crystallize for eighteen hours at 35° C. and then squeezing the liquid portion through filter cloth. The iodine value of this should not exceed 55 if the tallow be genuine, but in presence of cottonseed oil or cottonseed stearin a much higher result will be obtained. The solidifying-point (titre test) of the fatty acids should also be determined ; in the presence of the above-named adulterants it will be lower than 39° C. The phytosterol acetate test should also be applied (see p. 232).

Bone-fat leaves a variable but considerable proportion of ash on ignition. In 5 samples examined by Valenta the amount of ash ranged from 0·11 to 2·01 per cent. ; average 1·32. This ash contains much calcium carbonate and oxide. As pure tallow and most, if not all, other vegetable and animal fats leave a scarcely weighable trace of ash, the detection of bone-fat should not be difficult. Commercial bone-fat, according to Valenta's analyses, always contains a large percentage of free fatty acids ('4·8 to 26·5) ; adultera-tion with any quantity of such bone-fat would be excluded by the 4 per cent. limit for acidity. Neutral bone-fat has the characters of a good lubricant. Bone oil (bone-fat oleine) is said to be used for lubricating clocks and watches.

Horse-fat would probably communicate a yellow colour to tallow, would tend to make it soft, and would lower the melting-point of the fatty acids. This fat (as well as the above-mentioned) would lower the specific gravity of tallow at 60° F., which, however, is very rarely determined.

Paraffin wax, which is sometimes added to soft tallow, and usually reveals its presence by reducing the saponification value, can be determined by determining the unsaponifiable matter, which, in genuine tallow, does not exceed 0·4 to 0·6 per cent. The same process would enable *rosin oil*, if present, to be detected, and also *wool fat*.

Palmnut and *coconut oils*, besides raising the saponification value (which no other likely adulterant would do), would increase the Reichert value

and reduce the Hehner value. The commercial oils, which ar, usually very acid, would be excluded by the acidity test.

Valuation of Tallow.—By the soap and candle maker tallow is valued by the results of Dalican's titre-test (see p. 204). The 'titre' (*i.e.* the solidifying-point of the mixed fatty acids) of tallow intended for candle making should not be below 44° C. ; tallow of lower titre is used for soap-making (*Lewkowitsch*). The titre of tallow used for making railway axle grease is not of great importance, so long as it does not fall below 41° C.

Tallow Oil.

Few analytical data have been published for this oil. Allen gives the specific gravity at 60° F. as 0·916, and the solidifying-point as 0° to +6° C. (32° to 43° F.). Gill and Rowe state the sp. gr. at 100° C. to be 0·794. The oil should contain very little free fatty acid, and, if genuine, should have an iodine value of, probably, 55 to 60.

' *Ox oil* ' should be tallow oil expressed from beef tallow. ' *Animal oil* ' might contain the fat of other animals. Two samples of animal oil examined by one of the authors had a sp. gr. of 0·9187 at 60° F., iodine values of 59·7 and 60·4, and saponification values of 19·35 and 19·96 per cent. On cooling to 50° F., no crystals formed in three hours ; but on lowering the temperature to 46° F., crystallization commenced, and slowly continued until the oil ceased to flow on inclining the tube. The low percentage of acidity (0·25 per cent.) and the high viscosity (nearly equal to that of rape oil) of the samples were noteworthy features.

Lard Oil.

The **specific gravity** of genuine American lard oil at 60° F. ranges from 0·913 to 0·919, according to Schweitzer and Lungwitz.[1] Ten samples examined by Archbutt ranged from 0·9162 to 0·9181 ; of these, two described as American lard oil had the highest sp. gr. (0·9180 and 0·9181), the remainder (probably of home manufacture) did not exceed 0·9170. Allen states that the sp. gr. should not exceed 0·9160. Adulterants such as cottonseed and maize oils would raise the specific gravity.

The **Maumené thermal value** (determined as described on p. 260) of the ten samples tested by Archbutt ranged from 41° to 46°, practically the same as in the case of olive oil. This is, therefore, a very valuable test, since most oils likely to be added as adulterants, except mineral oil, would much increase the temperature reaction.

The **iodine value** of genuine lard oil varies considerably, owing to the variable proportion of olein. The interpretation to be placed upon the result of this test must, therefore, depend upon the congeal-ing-point of the oil. Schweitzer and Lungwitz, who have investigated this relation, determine the congealing-point as follows :—The oil is

[1] *Jour. Soc. Chem. Ind.*, xiv. (1895), p. 129.

poured into a wide-mouthed bottle, immersed in a freezing-mixture of ice and salt, and stirred vigorously with a thermometer ; the temperature is noted at which the oil shows the first sign of becoming cloudy. Any lard oil with higher iodine value than 70 should not show signs of cloudiness above 40° F. The lard oils having iodine values of from 60 to 64 are generally pasty at 40° F.

The **saponification value** of genuine lard oil is about 19·1 to 19·6. Adulteration with rosin oil, mineral oil, or rape oil would lower the value.

Rosin oil or mineral oil, if present, would be detected and determined by isolating the **unsaponifiable matter,** which in genuine lard oil is less than 1 per cent.

Cottonseed oil would probably be detected by Halphen's or Millian's **colour tests** ; sesamé oil by the furfurol test. Vegetable oils, as a class, would be detected by the phytosterol acetate test (p. 232).

Genuine lard oil contains no arachidic or lignoceric acids ; therefore, if these acids be found by **Renard's process** (p. 283), either earthnut oil, rape oil, or mustard seed oil must be present.

Neatsfoot Oil.

Commercial neatsfoot oil may include oil from the feet of sheep, pigs, horses and other animals, and is liable to extensive adulteration with vegetable oils, fish oils, mineral oils, and, doubtless, rosin oil. When properly prepared from fresh feet, this oil contains less than 0·5 per cent. of **free fatty acid** ; but the commercial oil, owing either to adulteration or to carelessness in manufacture, sometimes contains a very large percentage of acidity. According to E. Grant Hooper,[1] as much as 34 per cent. of free oleic acid has been found.

There is not sufficient data for defining the natural limits of variation of this oil ; the numbers in the table on p. 315, based upon results obtained chiefly by Lewkowitsch, and by Coste and Parry, must be regarded as approximate.

Seed oils, such as cottonseed and maize, also fish oils, would raise the **specific gravity, iodine value,** and **Maumené value.** Cottonseed oil would probably be detected by Halphen's and Millian's **colour tests** ; sesamé oil by the furfurol test ; and vegetable oils, generally, by the phytosterol acetate test (p. 232).

Mineral and rosin oil would be found in the **unsaponifiable matter,** which, in genuine neatsfoot oil, probably does not exceed 1 per cent.

Sperm Oil.

No means of distinguishing Southern and Arctic sperm oils, except by the smell and appearance, much less of detecting one when mixed with the other, can be said to be known. The most important differ-

[1] *Jour. Soc. Chem. Ind.,* xvii. (1898), p. 5.

ence between the oils appears to consist in the respect **melting-points of the mixed fatty acids**, but a sufficient number of authentic samples of each oil has not been examined to ascertain what this difference really amounts to. No difference exists in the refractometer values, Pearmain's figure +50, for Arctic sperm oil being obviously wrong. Samples of the two oils kindly examined for us by the late W. Chattaway in Jean's oleo-refractometer gave an identical reading of − 13. For the two samples referred to we are indebted to Mr. J. F. Ingleby of Hull, and it may be of interest to give here the complete results of the examination of these samples.

TABLE XCI.

Description	1 Finest Southern Sperm Oil	2 Deodorized Arctic Sperm Oil.
Colour, ...	Dark golden yellow	Golden yellow ; paler than No. 1.
Odour, . .	Slight fishy.	Fishy ; more pungent than No. 1.
Specific gravity at 60° F. (15·5° C.), .	0·8809	0·8787
Viscosity (absolute) at 60° F (15·5° C.),	0·3915	0·4148
Freezing-point, ...	Both practically 'set' in ice at 32° F. (0° C.)	
Refractometer value at 22° C., . .	− 13	− 13
Free acid, as oleic acid, %, . . .	1·2	1·6
Saponification value, %, . .	12·00	12·50
Iodine value, %, ...	84·4	81·5
Maumené thermal value : 50 grms. oil, 10 c.c. of 97% sulphuric acid ; ° C.).	46·0°	44·8°
Unsaponifiable matter(mixed alcohols),%.	39·1	39·7
Mixed Fatty Acids.		
Melting-point (Bach's method), ° C , .	21·4°	16·1°
Solidifying-point (Bach's method) ° C.,	16·1°	10·0
Mixed Alcohols.		
Colour, ...	Nearly white.	Nearly white.
Saponification value of acetylated product, %,	18·49	18·62

The problem, therefore, of detecting Arctic sperm oil in Southern sperm oil being, for the present at any rate, insoluble by chemical

methods, the two oils will be considered as identical in the following remarks.

The **specific gravity** of genuine sperm oil ranges from 0·878 to 0·884, and would be raised by the addition of any fixed oil or fat ; this could be corrected by the addition of light mineral oil, but not without lowering the **flashing-point**, which, according to Allen, is as high as 480' F. in the case of genuine sperm oil. Out of 93 samples of sperm oil tested by Veitch Wilson the flashing-points (closed test) of only three samples were below 410° F., viz. :—one sample 400° and two 390°. The others ranged from 410° to 485° F., and the averages were 457·5° F. for Southern sperm and 446·2° F. for Arctic sperm. There are pure mineral lubricating oils having the same specific gravity and viscosity as sperm oil, but their flashing-points are lower than 400° F.

The low **saponification value** of sperm oil is characteristic, but is not to be relied upon as a test of purity, since a mixture of a cheaper fixed oil with mineral oil could be made to have the same value. Lobry De Bruyn has found, however, that in sperm oil adulterated with such a mixture the presence of mineral oil can be detected by *Holde's test* (p. 219), since the higher alcohols formed by saponifying sperm oil do not separate at once on adding water, but remain for a considerable time dissolved in the soap solution.

The most reliable means of detecting the adulteration of sperm oil is to isolate and examine the **unsaponifiable matter**. Genuine sperm oil yields from 36·3 to 41·5 per cent. of unsaponifiable matter, consisting entirely of wax alcohols easily soluble in cold rectified alcohol ; if the unsaponifiable matter obtained from 5 grms. of a sample of sperm oil be normal in amount and completely soluble in 50[1] c.c. of cold alcohol of sp. gr. 0·834, the sample is most probably genuine. For further information as to the properties of the wax alcohols from sperm oil, see Table LXI. (p. 234) ; also page 230. For the analysis of mixtures containing sperm oil and mineral oil, see p. 245.

Porpoise and Dolphin Jaw Oils.

The remarkably high **Reichert value** is sufficient of itself to identify these oils. The high **saporification value** and low **iodine value** are also characteristic. The results obtained by the examination of a sample of Kelley's watch oil are given on p. 121.

D.—BLOWN OR THICKENED OILS.

Blown rape oil and blown cottonseed oil ('lardine') are usually pale-coloured and extremely viscous oils having a nauseous odour. The only natural oil which they at all resemble is castor, and from it

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[1] Not less ; see footnote on p. 230.

they are easily distinguished by their sparing solubility in alcohol. 1-2 c.c. of castor oil, if shaken in a test-tube with 10 c.c. of 90 per cent. alcohol, will dissolve easily, but the same quantity of blown oil remains apparently insoluble.

For the detection of blown oils in castor oil, see *Castor Oil* (p. 319). For their identification when mixed with mineral oil, the following characteristics are available, viz.:—the dark colour produced on saponifying them with alcoholic potash solution ; the high specific gravity at $\frac{100°}{100°}$ C. of their insoluble fatty acids (p. 185) ; the considerable proportion of soluble non-volatile acids formed by their saponification (p. 123) ; the comparatively low iodine value and high acetyl value of the insoluble fatty acids (see pp. 256 and 250).   The soluble non-volatile acids were determined by Thomson and Ballantyne by collecting the filtrate and washings from the insoluble acids, distilling to dryness and extracting the dry residue with ether.   After expelling the ether by evaporation, the acids were weighed and then titrated with standard alcoholic potash solution.   For the Reichert-Meissl value of blown oil, see p. 242.

Blown oils have not been sufficiently investigated to enable data to be given for distinguishing them with certainty one from another. Blown cottonseed oil may be recognized by the high melting-point of the fatty acids (41° C.), and may also be distinguished from blown rape oil by its higher saponification value, provided the oils compared have reached the same or nearly the same degree of oxidation, *i.e.* have been raised in specific gravity about the same number of units above the average gravities of the natural oils.   Thomson and Ballantyne have found, by experiments with such widely different oils as rape and sperm, that the specific gravity and iodine value simultaneously rise and fall in almost exactly the same ratio during oxidation.   Thus, a rise in the specific gravity of 1 unit in the third decimal place was accompanied by an average fall of 0·787 per cent. in the iodine value of rape oil, and 0·789 per cent. in that of sperm oil. The fall in the iodine value of the rape oil was, however, more rapid in the early stages of the blowing process, averaging 0·903 per unit rise of sp. gr. during the first five hours.   Similarly, the increase in the saponification value was more rapid at first, for, by the time the rape oil had risen in sp. gr. from ·9141 to ·9275, the saponification value had risen from 17·39 to 18·30, *i.e.* 0·067 per unit ; but after the oil was fully blown and had increased in sp. gr. to ·9·15, the saponification value had only risen to 19·49, or an average, during the whole period, of 0·044 per unit.

Blown oils should be examined for acidity in the same manner as the oils they are made from.   As stated on p. 122, the tendency of the blowing process is to increase the percentage of free acid.

E. - **MIXED LUBRICANTS**.

Mixed lubricants may be either oils or greases, and may or may not contain soap.   For the detection of soap, see section W, p. 303.

I. **Mixed oils and greases free from soap** may contain mineral oil, rosin oil, or coal-tar oil, together with a fixed oil, fat, or wax ; the fixed oil may be a blown oil.   An approximate analysis may frequently be made by Gripper's method (section D, p. 223).

A more exact analysis may be made by isolating and weighing the unsaponifiable matter (section E, p. 224), and then determining its properties and nature (section F, p. 228).   By recovering the mixed fatty acids from the soap solution, and submitting them to examination (section G, p. 235), the fatty ingredient of the mixture may frequently be identified.   Obviously, the problem becomes simplified when the mixed oil is purchased to a specification stating what the nature and proportion of the component oils must be.   For the analyses of mixtures containing sperm oil or wool fat and mineral oil, see p. 245.

II. **The analysis of oils and greases containing soap** is conducted in the following manner :

10 grms. of the sample are stirred with ether in a small beaker until dissolved or thoroughly disintegrated.   The liquid is then rinsed with ether into a separating funnel and shaken several times, with 10 c.c. each time of hydrochloric acid (sp. gr. 1·10) to decompose all soaps and extract the bases.   The ethereal liquid is then washed with water until free from acid.

Acid extract.- This contains the metals existing as soaps.   It is first washed with a little ether to remove mechanically mixed oil, the ether being added to the main ethereal solution.   The liquid is then placed in a beaker, covered with a clock-glass, and heated on a warm water-bath until the dissolved ether has boiled away.   It is then poured into a basin, evaporated to dryness on a steam bath, redissolved in hydrochloric acid and water, filtered, and the metal or metals which were qualitatively detected in the ash may be determined in the clear solution.

Ethereal solution.—This contains the neutral oil (fatty and mineral), together with all fatty and resin acids which existed in combination with the metal as soap.   In order to extract the fatty and resin acids, the solution is shaken with 50 c.c. of a 2 per cent. solution of caustic soda (10 per cent. caustic soda solution, 20 c.c. ; rectified spirit, 10 c.c. ; water, to 100 c.c.).   The shaking should be continued for half to one minute and be not too vigorous, lest an emulsion be formed.   After separation has taken place, the soda solution is drawn off into another separator, and the ethereal solution is further shaken with 10 c.c. quantities of the dilute soda solution until all fatty acids are extracted : it is then washed several times with water. The mixed alkaline extract is first shaken with a little ether, which is added to the neutral ethereal solution ; it is then acidified, and the

liberated fatty (and resin) acids are extracted with ether and weighed. The neutral ethereal solution is also evaporated and the residue weighed. We thus obtain : -

(a) *Metallic oxides, existing as soap.*

(b) *Fatty (and resin) acids existing in the free state and as soap.*— Determine the *free fatty acid* in a portion of the orignal sample as directed in section A, p. 216 ; if worth while, deduct this amount from the total, and multiply the remainder by 0·7 to reduce to anhydrides ; add the metallic oxides ; the sum is the amount of dry *soap*. *Rosin*, if detected by Liebermann's test, may be determined by Twitchell's method. *Phenols*, from coal-tar oil, if present (very rarely), would have to be separated from the fatty and resin acids by distillation with steam.

(c) *Residual (neutral) oil*. This may contain any or all of the following : —*mineral oil, rosin oil (coal tar oil), fixed oil, wax*, and, possibly, *free wax alcohols*. It must be analysed as directed above, p. 328, E, 1.

In addition, the grease may contain --

(d) *Water*. This is determined as directed in section Z, p. 305.

(e) *Non fatty ingredients* ; such as *plumbago, talc, sulphur*, etc — These will, for the most part, remain insoluble and be drawn off with the aqueous extract. They must be filtered off and examined separately.

(f) *Excess of base*. --This is detected and estimated by determining the combining weight of the fatty acids and ascertaining whether the amount of base found is more than sufficient to saturate them.

CHAPTER IX.

Introductory.—Although a great deal of information can be obtained by the chemical analysis of lubricants and by determinations of viscosity, specific gravity, flashing-point, etc., it is not always possible even for an expert to select with certainty from these tests alone the most suitable oil for a particular class of machine. There is no laboratory method of measuring the degree of 'oiliness' or 'greasiness' which a lubricant possesses, and upon which its value as a means of reducing friction at low speeds and under high pressures so greatly depends. It also very frequently happens that engineers in charge of machinery have no means of obtaining expert advice regarding the oils they use, and are compelled to rely upon such tests as they can themselves make. For this purpose, oil-testing machines have been invented with bearings so arranged that any desired load may be put upon them, the speed and method of applying the lubricant varied at will, and the frictional resistance, heating, etc., accurately measured.

Objects and Conditions of Mechanical Testing.— Mechanical tests of lubricants and friction surfaces may be made with two distinct objects in view, one being to measure the amount of frictional resistance to free motion offered by bearings lubricated in different ways or made of different metals or alloys, and the other to determine the relative oiliness or greasiness of the lubricants.

Useful hints concerning the *endurance* of oils may also be obtained by observing the changes which the friction undergoes after the oil has remained exposed for some hours to the air.

Specially designed machines have furnished data which have enabled Osborne Reynolds to place the mathematical theory of 'perfect' lubrication upon a firm basis, with the result that the part played by viscosity in the reduction of the frictional resistance between cylindrical journals and their bearings is clearly understood. Indeed, it may safely be said that mechanical testing machines have yielded to skilful operators information which is slowly but surely leading

engineers to substitute for old methods of lubrication new ones which give greatly increased efficiency.

A mechanical testing machine is thus, from a practical point of view, far from being a useless contrivance, and should be regarded as an indispensable part of the equipment of a modern oil-testing laboratory.

The more closely the conditions under which the oil is to work in practice are approached, the more satisfactory will be the results obtained ; for, from the point of view of frictional loss, every change which occurs in the load, in the speed of the journal, in the method of supplying the lub. icant, or in the rubbing surfaces, has an important effect upon the frictional resistance. In order, on the other hand, to determine the oiliness or greasiness of a lubricant, it is necessary to eliminate, as far as possible, results due to viscosity. 'Imperfect' methods of lubrication admit of this being done most satisfactorily, experiment having shown that whereas at low speeds greasiness is an all-important factor, in perfect lubrication at high speeds viscosity plays the more important part.

Thin films and low speeds are also the most suitable conditions under which to ascertain the effects resulting from changes in the nature of the metals in contact, as at high speeds a brass is generally lifted quite off its journal by the formation of the pressure film.

Design of Oil testing Machines.— Numerous forms of machine have been built and used for testing purposes, varying in design according to the effects which it has been desired to measure, and which may be summarized as follows :- -

(1) Comparative oiliness or greasiness of lubricants.

(2) Frictional effects due to viscosity.

(3) Effects resulting from different methods of applying the lubricant.

(4) Effects produced by different metals working in contact.

(5) Effects of temperature on friction.

(6) Effects produced by different loads.

(7) Effects produced by varying speeds.

A description of a few only of the different types of machine designed for ordinary testing work, or which have been used for experimental purposes, will here be attempted ; the nature of the tests which may be made with them being, in some cases, given. This can, however, only be done in an incomplete manner ; for the subject is an extremely complex one, each kind of machine requiring different treatment, and being capable of affording valuable information if placed in the hands of an operator who has a knowledge of the theory of lubrication and has had some experience in the management of machinery.

It must be remembered that every change of speed, load, method of lubrication, temperature, form of bearing, and condition of rubbing surface has some, frequently a considerable, effect upon the frictional resistance obtained with each lubricant, and, therefore, that the problems arising in the course of such experimental work are often

very intricate and difficult of solution. If, for instance, a number of oils tested under small loads fall in a particular order of merit as regards friction-reducing power, on testing them with heavier loads the order may be found to have entirely altered. Changes of speed produce even more marked differences, sometimes increasing and sometimes decreasing the friction. These points have been dealt with in some detail in Chapter IV., on 'The Theory of Lubrication.' Much, however, still remains to be learned concerning the frictional resistances of bearings when running at low speeds with different loads. This point will be briefly discussed in Chapter X., on 'The Design and Lubrication of Bearings.'

Mechanical testing machines vary greatly, not only in the shape of the contact surfaces, but also as regards the indications which they give concerning the degree of frictional resistance encountered. In some machines the rotating surface assumes the form of a wheel or drum upon which a bearing block is pressed. In others it is a disc, the flat side of which is pressed against a similar disc. But in the machines most commonly used the contact surface takes the form of a cylindrical journal a few inches in diameter, upon which rests a weighted bearing-block or brass.

It has been shown (p. 61) that the conditions under which lubrication can be effected with cylindrical rotating surfaces are quite different from those which obtain with discs or other plain surfaces. It will, therefore, be convenient to deal first with the rotating cylindrical or drum form of machine, and, subsequently, with machines that give the frictional resistances, etc., between discs and plain surfaces.

Cylinder or Drum Machines.—*Thurston's Oil-testing Machine.*— This machine, which is made by Messrs. W. H. Bailey & Co. of Manchester; is frequently used in England and America. It is convenient, and easily kept in order; for scientific work, however, it is hardly suitable. Two sizes are made: one, a small machine, occupying but little space and requiring very little power to drive it; and another, of much larger form, suitable for railway work.

Of these, the larger machine only will be described. It has a cylindrical journal against which work two brasses, one above and the other below. Slung from the upper brass is a hollow pendulum containing a strong spring, the upper end of which lifts the bottom brass against the journal, whilst the lower end depresses the pendulum and helps to weight the upper brass.

Fig. 75 is a side elevation, with brasses and pendulum in section, and fig. 77 is a photo-print of this machine as used by the authors. Fig. 76 is a front view of part of the machine drawn to a larger scale. The hollow shaft A, driven by a cone pulley B, is mounted on a strong cast-iron stand, the forked ends of which form the bearings upon which it runs. One end of the shaft projects beyond the bearing and is fitted with a bush C, on the outside surface of which the oil tests are made. This enables various metals to be used as bearing surfaces, for the bush can be removed and another put in

its place. The box EE, forming the head of the pendulum, holds
the two bearing brasses DD, on which the pendulum is slung from
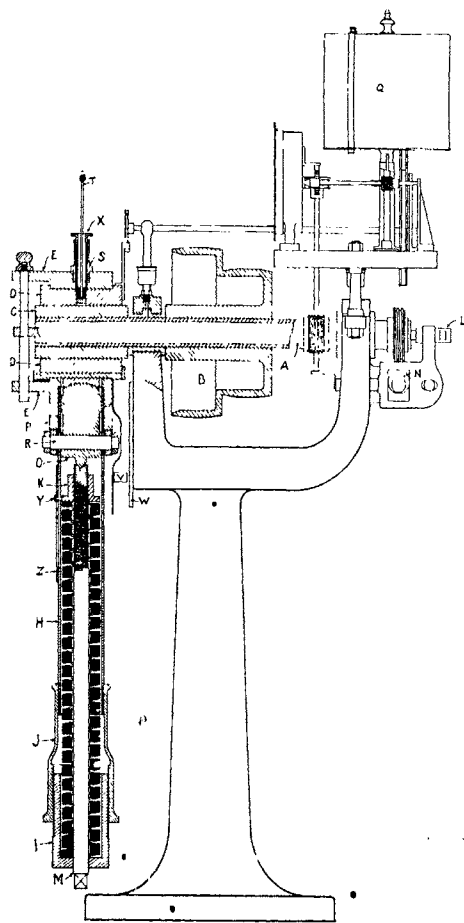
FIG. 75.

the journal. In order to enable the operator to vary the pressure
of the brasses against the journal at will, the pendulum is constructed
as follows:—A brass tube, H (figs. 75 and 76), is screwed into the

axle-box E, which passes round the journal and holds the bearings D
in position. In the upper part of this tube is loosely fitted a distance
piece O, which, by the action of a strong spring below it, forces the
under brass against the journal. The end of the spring does not
press directly against the distance piece, but upon a screwed washer,
K, threaded upon a rod M, which has a square end, by means of
which it can be rotated. At its lower end the spring rests upon a
cap, I, screwed to the tube H, by which the stress on the spring is
brought to bear upon the upper bearing D, as well as on the lower
one. To compress the spring and increase the load on the bearings,
the square end of the rod M is rotated, which lowers the washer K,
to which is fixed the index finger Y. A graduated scale, Z, screwed
to the tube H, shows the weight per square inch and the total weight
on the brasses for every position of K. A ready means of taking
the pressure off the brasses is furnished by the nut P, which can be
screwed down until the key R, against which it presses, separates the
distance piece O from the bearing.

It is evident that any friction between the brasses DD and the
journal C will cause the pendulum to move in the direction of
revolution of the shaft, and the greater the friction the further will
the pendulum swing, the angular movement being indicated by the
pointer V moving over the arc W (see fig. 76). As the moment of
resistance of the pendulum varies with its weight and the position of
its centre of gravity, it is possible to vary very considerably the
scale of total frictional resistances marked on the arc W. When an
open scale is required, the castings I and J are suitably reduced in
weight, as shown in the figure; a counterbalance can also be placed
on a pillar screwed into the top of the axle-box E. Of course, each
alteration of the position of the centre of gravity of the pendulum
necessitates a corresponding change in the graduation of the scales
W and Z, and for this reason it seems preferable to graduate the arc
in degrees instead of in total frictional resistances (see p. 339).

The lubricant can be supplied to the journal by means of pads,
fixed in the sides of the axle-box, the method of supplying the oil to
the pads being varied according to the conditions of lubrication
under which it is desired to experiment. Another method, used by
the authors, is shown in fig. 76. a a are glass tubes passing through
corks fixed in holes in the sides of the axle-box. Each tube is drawn
down to a fine orifice, through which a double strand of cotton wick,
b, is passed, held by means of a looped platinum wire, w. The tube
is filled with the oil to be tested, which is conveyed through the wick
on to the journal. By varying the size of the orifice, the rate of
feed of the oil can be altered at will. The oil fed in this way on to
the journal does not spread itself evenly along the upper brass, but
tends to collect at the middle ; and at high speeds, if the feed of
oil be rapid, it tends to collect in drops, and to fall away from the
journal without wetting it.* It was found that this could be pre-
vented by placing a knitting needle, c, in the angle between the brass

and the journal. The knitting needle, which is held in position by the tension of the oil-film, rotates rapidly, and spreads the oil from end to end of the brass. Two small hooks, k (the front one only shown), fixed to the ends of the brass prevent the needle from falling away when the machine stops, or if the tension of the oil film should become momentarily weakened. To spread the oil along the lower brass, a narrow strip of sheet brass, p, is soldered near one edge, so as to form with the journal a channel which collects the oil. This lower brass, in the machine used by the authors, is crescent shape in
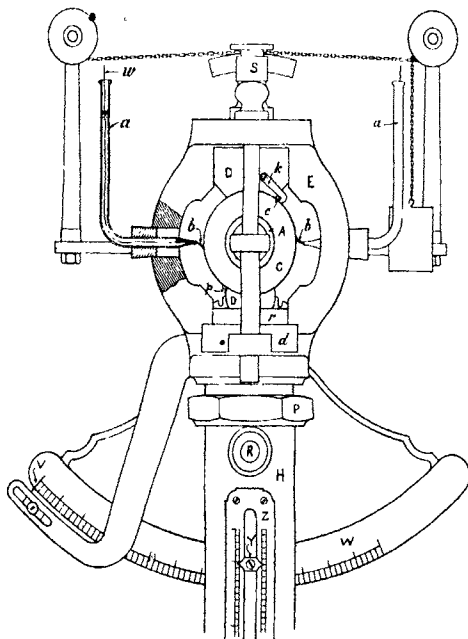
Fig. 76.

section, and is supported in a well lubricated steel cradle, r, which allows a little sideplay in the axle-box, and enables the friction surfaces to place themselves in that position which gives the greatest carrying power. Suitable grooves cut in the steel cradle collect the surplus oil which falls from the journal and brasses, and conduct it into the trough d (fig. 76).

To assist in distributing the lubricant evenly over the journal, and to prevent both it and the brasses from wearing in ridges, the

latest form of Thurston's machine is fitted with an eccentric N, fig. 75, actuating the rod L, which slowly moves the brasses backwards and forwards along the journal. With this device attached, the readings obtained by making a series of tests of the same lubricant show fewer and smaller discrepancies than can be obtained when the brass has no lateral play.

In the machine as usually supplied, a thermometer, the bulb of which is let into the metal of the upper bearing, measures the temperature to which the latter is raised by the friction. In the machine used by the authors, the hollow brass pillar, S (fig. 75) is screwed into the top of the axle-box, and through 'this a thin steel tube, X, closed at the lower end, is passed into a conical hole in the upper brass into which the end of the steel tube fits closely. In this tube an ordinary glass chemical thermometer, T, is placed, the bulb of which is immersed in mercury which fills the lower end of the steel tube. When it is desired to remove the pendulum from the testing journal, the steel tube X is taken out, and a brass cap with a ring at the top is screwed on to the brass pillar S. By means of an attachment from a small overhead travelling crane, the pendulum may thus be easily moved off and on the journal.

To the pendulum and stand is sometimes attached a cord or chain, of such length that the pendulum cannot swing beyond the desired limit.

The machine should be driven at a very regular speed, preferably by an electric motor, and such gearing should be used as will enable it to be run at a variety of speeds; for, with good lubrication we may, roughly, consider that at high speeds and moderate loads it is the viscosity which controls the frictional effects, whilst with low speeds and heavy loads the efficiency of the lubricant depends upon its oiliness or greasiness, as well as upon its viscosity.

To the latest form of this machine there is attached an automatic recording apparatus, which registers on a sheet of ruled paper the number of revolutions made by the journal and also the frictional resistance at each moment. The paper upon which the record is drawn is placed upon a drum, Q (fig. 75), revolving once for every 100,000 revolutions of the journal. Against the paper rests a pen, actuated by the pendulum as it swings from the vertical. In the machine used by the authors a second speed gear has been added for slow speed tests, capable of revolving the drum once for every 120 revolutions of the journal, so that the diagram paper is moved a quarter inch for one revolution of the journal. A counter is fixed on the machine in a convenient position, to indicate the number of revolutions made by the journal.

The greater portion of the load placed upon the test bearings results from the compression of the central spring, and is equally distributed between the upper and lower brasses In addition, however, to the pressure resulting from the stress of the spring, the upper brass C, when the swing of the pendulum is small, has to carry

the weight of the pendulum as well.   When this r. light, and the
pressure on the spring considerable, no serious error results from
taking the load on the bearings as being distributed evenly between
the two brasses.   Although, by grasping the journal between two

Fig. 77.

brasses, and putting on the load by compressing a spring, some errors
are introduced, the arrangement has the advantage of reducing the
pressure on the supports of the journal, and all risk of overheating
the fixed bearings is avoided.

Several methods of calculating the area of contact of a brass have been adopted. The plan commonly followed has been to multiply the length of the brass (b) by the diameter of the journal ($2r_0$); $2r_0b$ is then the projected area of the bearing on a diametral plane, or, as it is commonly called, the nominal area. But it is impossible, except with light loads, to make a bearing run satisfactorily when the brass embraces as much as one-half of the journal. In practice, the sides have to be put away until the actual arc of contact is only one-fourth or one-fifth of the circumference; and as at all ordinary speeds, with good lubrication, the friction is nearly proportional to the actual contact area, it is better to substitute actual for nominal areas by multiplying the length of the arc of contact a by that of the brass b.

Thurston graduates the scales on his machine on a nominal area basis; however, from the following formulæ the scales can be graduated to agree with actual areas of contact, and from them the true coefficient of friction, etc., can be obtained.

Let r = radius from centre of journal to centre of gravity of pendulum.
  r_0 = radius of journal.
  W = weight of pendulum.
  a = width of brass (*i.e.* length of arc of contact).
  b = length of brass.
  P = total pressure of brasses on journal.
  p = pressure per sq. in.
  T = load on spring.
  θ = angle between pendulum and perpendicular through axis.
  μ = coefficient of friction.
  F = total frictional resistance.

When θ is equal to $90°$, $Wr = Fr_0$.   .   .   (1)
When it is equal to any other angle, $Wr \sin \theta = Fr_0$.   .   (2)

Therefore, $$F = \frac{Wr \sin \theta}{r_0}$$.   .   .   .   (3)

From equation (3) the graduations on the arc W are usually marked off so as to give the total frictional resistance F for any angle, but as, when the spring is compressed, the centre of gravity of the pendulum moves downwards, and the length of r therefore increases, these graduations can only be strictly correct for one position of the spring.

When the pendulum is a heavy one, and the compression on the spring is such that the load on the brass is small, the load on the upper brass is, at all small inclinations, $P_1 = T + W$.   .   .   .   .   (4)
and on the lower brass, $P_2 = T$.   .   .   .   .   .   (5)

When T is large and W is small, it is sufficiently accurate to make
                  $P = 2T + W$.   .   .   .   .   (6)
and from this the left hand side of the scale N is graduated.

Under similar circumstances, the pressure per sq. in. is $p = \dfrac{P}{2ab} = \dfrac{2T + W}{2ab}$ (7)

From this equation, the graduations on the right hand side of the index plate are deduced.

The readings given by the index plate N and the arc W enable the coefficient of friction to be calculated directly, for

$$\mu = \frac{F}{P} = \frac{\text{Reading given by arc W}}{\text{Reading given by index N}}$$.   .   (8)

When experimenting with small loads on this machine, it must be borne in mind that the load on the upper brass is always greater than on the lower one. Under such circumstances, the maximum load is given by equation (4)

and the pressure per sq. in. is $p = \dfrac{P_l}{ab} = \dfrac{T+W}{ab}$.   .   .   .   .   . (9)

It is impossible always to measure accurately the friction due to the upper and lower brasses respectively. When the lubrication is good, and the speed of rubbing over 3 feet per minute, the friction is proportional to the area of the brass in contact with the journal and independent of the load, but when the speed is small this is not the case, and it is impossible to obtain *accurately* the coefficient of friction of either the upper or lower brass.

As stated on page 334, the graduations on the arc W, when marked so as to give the total frictional resistance F, are subject to a small error, due to the fact that the length of r is increased by compressing the spring. Also, any alteration of the weight of the castings J and I would render these graduations useless. The authors therefore prefer to graduate the arc in degrees, and the index N in lbs. of spring pressure, and to construct a table from which the coefficient of friction can be read off corresponding to any angle of pressure. As an example, the following particulars of the machine used by the authors are given, but of course they will not apply to any other machine, unless of exactly the same dimensions, weight, etc.

TABLE XCIA.

Value of W, .   . 159·5 lbs.

 ,, r_m . . 1·875 inches.

 ,, r, . . $\begin{cases} \text{At 0 lbs. pressure of spring} = 14\cdot64 \text{ inches.} \\ \text{At } x \ (1000) \text{ lbs. } \text{,,} \quad = 14\cdot64 + x(0\cdot026) \text{ inches.} \end{cases}$

 ,, ab, . $\begin{cases} \text{Upper brass} = 13\cdot30 \text{ sq. inches.} \\ \text{Lower ,, } = 13\cdot13 \text{ ,,} \end{cases}$

 ,,   T, .   . At 1000 lbs. on index N, the load due to pressure of spring = 500 lbs. on each brass.   Therefore,

Scale Reading (lbs).	Total Pressure (P) of brasses on Journal.	Pressure per sq. inch (*p*).	
		On Upper Brass.	On Lower Brass.
1,000	1159·5	49·6	38·1
2,000	2159·5	87·2	76·2
3,000	3159·5	124·8	114·2
4,000	4159·5	162·4	152·3
5,000	5159·5	200·0	190·4
6,000	6159·5	237·6	228·5
7,000	7159·5	275·2	266·6
8,000	8159·5	312·7	304·6
9,000	9159·5	350·3	342·7
10,000	10159·5	387·9	380·8

$$P = \frac{Wr \sin \theta}{r_0} = \frac{159 \cdot 5 \, r \sin \theta}{1 \cdot 875} = 85 \cdot 07 \, r \sin \theta. \quad \text{Hence,}$$

Scale Reading (lbs).	Value of F.	Value of $\mu = \dfrac{F}{2T + W}$
1,000	1247·64 sin θ	1·076 sin θ
2,000	1249·85 ,,	0·579 ,,
3,000	12ʳ2·06 ,,	0 396 ,,
4,000	1254·27 ,,	0·301 ,,
5,000	1256·48 ,,	0·243 ,,
6,000	1258·69 ,,	0·204 ,,
7,000	1260·91 ,,	0·176 ,,
8,000	1263·12 ,,	0·155 ,,
9,000	1265·33 ,,	0·138 ,,
10,000	1267·54 ,,	0·125 ,,

From the above, Table XCIв. has been constructed.

TABLE XCIв.

Deflection of Pendulum (degrees)	Total Pressure on Scale N. (Thousands of Pounds)									
	1	2	3	4	5	6	7	8	9	10
	Coefficients of Friction.									
0 1	·0019	·0010	·0007	·0005	·0004	·0004	·0003	·0003	·0002	·0002
0·2	·0038	·0020	·0014	·0010	·0008	·0007	·0006	·0005	·0005	·0004
0·3	·0056	·0030	·0021	·0016	·0013	·0011	·0009	·0008	·0007	·0007
0·4	·0075	·0040	·0028	·0021	·0017	·0014	·0012	·0011	·0010	·0009
0·5	·0094	·0050	·0034	·0026	·0021	·0018	·0015	·0014	·0012	·0011
0·6	·0113	·0061	·0041	·0031	·0025	·0022	·0019	·0016	·0014	·0013
0·7	·0132	·0071	·0048	·0036	·0029	·0025	·0022	·0019	·0017	·0015
0·8	·0150	·0081	·0055	·0042	·0034	·0029	·0025	·0022	·0019	·0017
0·9	·0169	·0091	·0062	·0047	·0038	·0032	·0028	·0024	·0022	·0020
1·0	·0188	·0101	·0069	·0052	·0042	·0036	·0031	·0027	·0024	·0022
2·0	·0376	·0202	·0138	·0105	·0084	·272	·0061	·0054	·0048	·0044
3·0	·0563	·0303	·0207	·0157	·0126	·0107	·0092	·0081	·0072	·0065
4·0	·0751	·0404	·0276	·0210	·0169	·0143	·0123	·0108	·0096	·0087
5·0	·0938	·0505	·0345	·0262	·0212	·017.	·.153	·0135	·0120	·0109
6·0	·1125	·0605	·0414	·0314	·0254	·0213	·0184	·0162	·014.	·0131
7·0	·1311	·0705	·0482	·0366	·0296	·0248	·0214	·0189	·0168	·0152
8·0	·1498	·0805	·0551	·0419	·0337	·0284	·0245	·0216	·0192	·0174
9·0	·1683	·0905	·0619	·0471	·0379	·0319	·0276	·0243	·0216	·0196
10·0	·1868	·1005	·0688	·0523	·0421	·0354	·0306	·0269	·0240	·0217

Before using a new machine, it is desirable to test the spring and verify the graduations on the arc W and the scale N, if correct results are desired. The pointer which indicates on the arc W the deflection of the pendulum should be a knife edge, and should be attached to the axle-box and not to the brass tube, since the latter rotates slightly when the nut P is turned. It is also necessary that this pointer should be capable of adjustment, in order that it may be

made to point accurately to zero when the pendulum comes to rest after swinging freely, which free swinging of the pendulum is brought about in the following manner. The journal is well lubricated with the oil to be tested, and is run for a few seconds at the speed of about 100 revolutions per minute, the pendulum being allowed to hang by its own weight, and all pressure on the journal due to the spring being removed. An oil-film between the upper brass and the journal having been thus established, the machine is stopped : the pendulum, being now supported on the oil-film, will swing freely for several seconds before the oil is squeezed out, and, if correctly adjusted, the pointer will make approximately equal and gradually diminishing excursions on either side of the zero before coming to rest on the zero point.

Method of Working.—As already stated, in the machine used by the authors the arc W is graduated in degrees, and the scale N in pounds of spring pressure. Plain paper is used on the recording drum, and, before making each test, a base line is drawn upon the paper by rotating the drum against the pen with the machine at rest and the pointer at zero. At the end of the test, the area enclosed between the curve and this base line is measured by means of a planimeter if the curve is irregular, and thus the average deflection of the pendulum is easily determined and the friction coefficient read off from the table. The following simple rules are followed in making each test :—

1. See that the pointer is accurately adjusted to zero on the arc when the pendulum is hanging freely.

2. With the machine at rest, and the pointer at zero on the arc, lower the pen on to the paper, and draw a base line by rotating the drum. Then raise the pen off the paper.

3. Screw up the spring, with the brass nut, P, slack, until the desired pressure is attained, then screw the nut down until the pressure is taken off the journal. Start the machine, and adjust the lubricators so as to give the required oil-feed. Then slack the nut sufficiently to bring the pressure of the spring on to the journal, and run the machine at a fair speed until the brasses are well oiled and are nearly at the extreme front end of the journal. Then adjust the speed to that required for the test, and, as soon as the brasses reach the extreme front end of the journal,[1] drop the pen and commence the test.

4. *Starting.*—Before starting the machine, see that the pressure of the spring is off the journal, and that the pen is raised off the paper.

5. *Stopping.*—Before stopping the machine, raise the pen off the

[1] The friction is sometimes different at the front and back ends of the journal. Therefore it is desirable, especially when making slow speed tests, to commence always at the same point.

p per.   Before releasing the pressure of the spring, also raise
th pen off the paper.

6. *Removing pendulum from journal.* - Before removing the
pendulum from or replacing it upon the journal, take care to
release the pressure of the spring, either by screwing down
the nut P or by unscrewing the rod M.

Before testing a fresh sample of oil, the pendulum must be removed
from the journal, and the brasses and journal must be wiped
thoroughly clean, using first of all a sponge cloth and afterwards a
soft duster, and taking care to leave no lint upon the surfaces.   The
lubricators, *a a*, fig. 77, are cleaned by rinsing with ether or benzine,
then warmed, and aspirated with air until every trace of the solvent
has been expelled.   They are then filled with the oil to be tested, a
few drops of the oil are also placed upon the journal and brasses and
spread over the surfaces with the clean finger, and the pendulum
is replaced upon the journal.   Then the machine is run for a few
minutes with a free oil-feed to flush away the remaining traces of the
oil last tested, and the test of the new oil is commenced.

Great care must be taken not to allow the brasses and journal to
run dry and seize locally.   Should this happen during any test, the
friction of the surfaces will be so much increased in succeeding tests,
even with the same oil, that the results will not be comparable with
the previous tests.   In fact, the effect upon the frictional resistance
of the surfaces caused by very small changes in their shape or con-
dition is so great, especially at slow speeds and at high pressures,
and with bath and pad lubrication, that each sample of oil tested in
the machine must be compared with results obtained by testing some
standard oil immediately before, and, preferably, again immediately
after, the sample has been tested.   If the two tests obtained with
the standard oil do not agree, one cannot be certain that differences
observed between the sample and the standard may not be due to
the frictional resistance of the surfaces having altered during or
between the tests.

When commencing to use a new machine or new brasses, the proper
bedding of the brasses to the journal is very important, and with new
brasses is very tedious.   As the most rapid wear takes place at low
speeds and under high pressures, we have found it best, when bedding
new brasses, to run the machine under these conditions with a
mineral lubricating oil of moderately low viscosity (*e.g.* 900/7 oil),
removing each brass at intervals of about two hours and very care-
fully scraping the high places, finally rubbing them down with the
finest emery paper until the brass is seen to be bearing all over.
Another important point is to have a very hard surface on the testing
journal.   If the journal be made of soft steel, particles of brass torn
off the bearings are apt to become embedded in the steel : these
gradually gather more brass as the journal revolves, and eventually
sufficient is collected to cause local seizing to take place, and the
surface of the brass becomes ruined.

To secure low frictional resistances, and to obtain res¹¹s almost wholly dependent upon the viscous properties of the lub.cant, the brasses should each cover about one-fourth of the circumfer :nce of the journal ; no oil-ways should be cut in their surfaces, but the lubricant should be supplied by means of pads or other lubricators placed at the sides of the journal.   The speed of rubbing should not be less than 100 feet per minute.   When these conditions obtain and the load is not too great, it has been demonstrated that the friction is practically proportional to the viscosity of the oil, and is entirely independent of the nature of the contact surfaces or the oiliness of the lubricant.   It is only with fairly viscous oils, light loads, and good lubrication, that the oil pressure-film forms properly at speeds lower than 100 feet per minute.   It will, of course, be understood that different oils will heat differently, and that the viscosity of the *heated* oil film must be taken for comparison with the frictional effect, for the test to be a fair one. On this account, when trials are made in such a manner that the friction results entirely from the viscosity of the liquid, the oil which at ordinary temperatures is most viscous does not always give the greatest friction, for the lubricating film is heated several degrees above the temperature of the surrounding metals by the work done, and its viscosity is thereby reduced.   Mineral oils tested against animal or vegetable oils of the same viscosity will thus sometimes give the lower friction, for the former lubricants, when heated, lose their viscosity somewhat more rapidly than do the latter (see pp. 168, 169).   Tests of this kind by no means show which is the best lubricant, and need seldom be made, for the actual viscosity of an oil and the effect produced by increased temperature can be more satisfactorily ascertained with the viscometer.

The legitimate practical result obtained by mechanical oil-testing machines is, as has already been pointed out, the determination of the comparative oiliness or greasiness of liquids and soft solids ; properties upon which the power of lubricants to prevent the abrasion and wear of contact surfaces largely depend.   The method which has been most generally adopted to determine such properties has been to imperfectly lubricate the bearings, and thus allow the surfaces to approach each other so closely that the oil pressure-film cannot form properly.   It is essential that the bearing surfaces should come into close juxtaposition, if we are to obtain a correct estimate of the value of different brasses, bronzes, and white metals, for these metals are only used to enable the bearing to carry its load without suffering abrasion when the conditions of running are such that the oil pressure-film, maintained by the viscosity of the lubricant, cannot form, and the surfaces approach each other closely.   For tests of this kind, the brasses should be allowed to extend over only about one-fifth or one-sixth of the circumference of the journal, and the lubrication may be supplied by means of lubricators or well-moistened pads at the sides.

Supposing two oils are to be compared with one another, testing

should be commenced at a speed of about nine inches to one foot per minute, and at the highest pressure which the oil and bearing will safely carry without seizing. It will be found, as a rule, that this pressure will be greater the higher the viscosity of the oil. Repeated tests should be made with the same oil, at the same pressure and speed, until successive curves, each corresponding to one complete to-and-fro movement of the brasses along the journal, become practically uniform. Three curves should then be measured with the planimeter and the average friction calculated. Curves obtained at this slow speed 'and at high pressures will probably be very irregular in shape, owing to variations in the frictional resistance, due to slight irregularities of the surface ; but, if a smooth curve be obtained it will not, of course, be necessary to use the planimeter, and the average deflection of the pendulum can be read off directly from the scale on the arc. If the friction show a tendency to diminish continuously, the brasses are probably not properly bedded to the journal, and the process of wearing them down must be continued.

Having obtained satisfactory curves from one oil, the journal, bearings and lubricators should be cleaned, and the other oil tested in a similar manner. Further tests should then be made with both oils, first at from 5 to 7 feet per minute, and then at 100 feet per minute. It will be found that, as the speed is increased, greater loads can be put upon the bearings. At these higher speeds, also, the friction will be less variable, the curves traced on the diagram will be more regular in form, and an average deflection of the pendulum can usually be read off directly on the arc.

In the slow-speed tests, the temperature of the bearings and journal will scarcely be affected by the friction during the test, but in the tests made at a speed of 100 feet per minute, the rise of temperature of the brasses will be comparatively rapid and may be made the basis of a test. For this purpose, the machine should be allowed to run until a definite temperature of, say, 80° F. is reached. The pen should then be dropped on the paper, the time noted, the counter index read off, and the average deflection of the pendulum observed and recorded. When the thermometer indicates 85° F., the time and the average deflection of the pendulum should again be recorded. These observations should be repeated at intervals corresponding to every five degrees rise in temperature, until either the temperature has risen to, say, 140° F., or the journal has performed 30,000 revolutions. Some tests made in this way are recorded in Table XCIc.

The results recorded in Table XCII. were obtained by testing different oils at a nearly uniform speed of 7·2 feet per minute, and under a constant average load of 271 lbs. per square inch of bearing surface (measured along the arc of contact). The tests were made consecutively, in the order stated.

TABLE XCIc.

				American Mineral Oils.			Russian Mineral Oil.
Description of Oil.	Olive.	Lard.	Rape.		Solar Red Engine	Special Red Engine.	
				"900/7"			
Specific gravity at 60° F.,	0·916	0·917	0·911	0·906	0·917	0·936	0·907
Viscosity at 60° F.,	0·98	0·98	1·16	1·11	2·06	3·0	3·48
Number of revolutions,	30,000	30,000	30,000	30,000	30,000	29,196	32,000
Temperature rose from 80° F. to,	108·5°	105·0°	108·5°	106·5°	115·2°	113·8°	117·2°
Coefficient of friction fell during test { from	·0051	·0044	·0055	·0016	·0074	·0078	·0085
to	·0031	·0030	·0035	·0031	·0037	·0037	·0037

Tests made at a Speed of 981 feet per minute

TABLE XCId.

SPEED, 7·2 feet per minute.
AVERAGE LOAD, 271 lbs. per square inch of bearing surface.

Test No	Oil Used.	Viscosity at 60 F.	Average Coefficient of Friction	Temperature of Bearings.
107	American mineral oil (0·936),	3·0	·0035	63° F.
108	Russian mineral oil (0·907),	3·48	·0035	65° F.
109 {	Russian mineral oil, 75%, Rape oil, 25/,	...	·0023	65° F.
110 {	Russian mineral oil, 25%, Rape oil, 75%,	...	·0037	65° F.
111	Rape oil (0·914),	1·16	·0012	66·5° F.
112 {	American mineral oil, 75% Rape oil, 25%	...	·0034	62° F.
113 {	American mineral oil, 25%. Rape oil, 75%,	...	·0033	65° F.
114 {	Russian mineral oil, 75% Rape oil, 25%	...	·0025	66·5° F.

The mixtures used in five of the tests were made with the same samples of mineral and rape oils as were used for the remaining three tests. It will be observed that, at the comparatively slow speed used, both the mineral oils gave lower coefficients of friction than the rape oil, owing to their much higher viscosity, but the

mixtures gave lower coefficients than either of the pure oils. It is also remarkable that the mixture of Russian oil with 25 per cent. of rape oil gave a much lower friction than the mixture with 75 per cent. of rape oil, and the same result was obtained on repeating the test ; see No. 111. The almost identical results obtained in tests Nos. 109 and 111 prove the comparative accuracy of the series.

The results recorded in Table XCIE. show, in an interesting manner, how the friction changes with the load at low speeds, how much more rapidly it changes at a speed of less than one foot per minute than at nine times that speed, how greatly an increase of speed may affect the friction when the load is constant, and also what an important influence the viscosity of the oil has upon this as well as, generally, in reducing the friction at low speeds. The marked differences in friction-reducing power at these low speeds between the three fixed oils, and between rape oil and a mineral lubricating oil of very nearly the same viscosity, will also be noted.

TABLE XCIE.

	Olive Oil	Lard Oil.	Rape Oil	American Mineral Lubricating Oils				Russian Mineral Lubricating Oil.
Specific Gravity at 60° F.,	0·916	0·917	0·914	0·906	0·917	0·936		0·907
Viscosity at 60° F.,	0·98	0·98	1·16	1·11	2·06	3·0		3·5

Speed. Feet per Minute.	Load. Lbs. per square inch of Bearing Surface.	Coefficients of Friction.						
0·8	120	·0055	·0041	·0029	·0027	·0021	·0015	·0011
,,	139	·0150	·0128	·0043	·0214	·0042	·0012	·0012
7·0	139	·0015	·0012	·0012	·0018	·0027	·0036	·0033
,,	157	·0018	·0016	·0016	·0021	·0026	·0039	·0031
,,	176	·0023	·0020	·0018	·0033	·0035	·0042	·0033
,,	195	·0040	·0034	·0019	·0035	·0042	·0042	·0034
,,	2r̄ʲ	·0046	·0043	·0032	·0058	·0055	·0057	·0053

Useful comparisons of oils can thus be made with Thurston's machine, but we are bound to admit, as the result of much experience, that when facilities exist for making complete examinations of oil by viscosity and other laboratory tests the results obtained by the machine can frequently be predicted, and are, therefore, of limited value. The fact is, that the machine tests which are most

valuable are those made under conditions which are ve y liable to damage the friction surfaces, and which, therefore, make accurate comparison between different oils extremely difficult t obtain. For instance, it would be useful to know, in comparing oils one with another, which oil will carry the greatest load without seizing ; but if, in making such tests, the bearing surfaces should accidentally seize, even momentarily, damage may be done to them which would take a long time to repair, and which would necessitate the repetition of the tests which had been made previously to the damage.

Thurston states that his machine may be used for the purpose of ascertaining the gumming properties of lubricants, and also their durability. No doubt with care some idea on these points may be obtained by the use of mechanical testers, but such tests are usually better made by physical and chemical methods.

Many lubricants when exposed to the air take up oxygen and become thick, *i.e.* they gum. This change in the viscosity may be scarcely appreciable when the liquid is kept in bulk, but when it is spread over a bearing as a thin film and exposed to the air, it may rapidly become a sticky mass and cease to lubricate. Although the extent to which this change takes place can be more satisfactorily measured by methods which have already been fully described (p. 265 *et seq*), useful information may sometimes be gained by measuring the effect produced upon the friction coefficient. The bearings should be lubricated with just sufficient oil to wet them well and yet not run off. The journal is then run at a speed of about 100 feet per minute with a very light load, and the friction and temperature noted when they have ceased to vary appreciably. Both brasses are then removed, and the contact surfaces, protected from dust and dirt, are allowed to remain exposed to the air for a day or two. The brasses are then replaced in the machine and a test made as before. If the oil has thickened, the friction and heating will be greater than before. Tests of this kind are, however, very likely to injure the friction surfaces, and it is, therefore, very questionable whether it is worth while to make them.

Many lubricants which are liable to gum may also become acid and attack the bearing surfaces. Metallic soaps are thus formed, which dissolving in the lubricant, cause it to thicken. Mineral oils, which do not gum by oxidation, may contain light constituents which evaporate and leave thicker residues behind. For these and other reasons. an increase in the friction and temperature of a bearing after standing for a time does not prove that the oil has really gummed by oxidation.

For tests of durability, the lubricant may either be supplied continuously in such small quantities that it shall not run off the bearing, but shall yet wet it well, or pads soaked with a definite quantity of oil may be lightly pressed against the sides of the journal. The machine is then allowed to run until the friction and temperature begin to rise unduly. For some time after starting, the lubricant

remains in good condition, the temperature becomes steady, and the friction reaches a minimum. As soon, however, as the lubricant thickens, or becomes charged with material worn off the bearings, or with soaps resulting from its acidity, the friction and temperature begin to rise. The particular oil the smallest quantity of which will keep the bearing in good condition, is considered the best to use for the particular load and speed of rubbing.

When the lubricants are good and are little affected by the atmosphere or the metallic surfaces upon which they rest, they continue to keep the bearings cool much longer than when they are acid, oxidizable, or contain light and volatile constituents.

Smith's Friction-Testing Machine. — This machine (fig. 78), designed by Prof. Robt. H. Smith, is used in the engineering laboratories of the University of Birmingham. It somewhat resembles a Thurston machine, the pendulum of which is suspended in a horizontal position from above its centre of gravity, thus removing from the journal all the pressure due to the weight of the pendulum and its contained parts.

The testing journal, B, which can be made of any desired diameter, is screwed into the end of the shaft A, driven by the coned pulleys, P P P. The bearings, C C, are pressed upon the journal by means of a powerful spring, enclosed in the barrel D, the spring being compressed and released by means of the screw E, the worm-wheel F, and the worm and hand wheel gearing V. The weight of the barrel, spring, bearings, etc., is supported by means of the suspension rod G, lever H, and weight W, the position of the latter being adjusted so as to keep the lever floating between the stops I I.

The journal friction and torque is balanced by the two equal and opposite forces exerted by the two ends of a fine whip-cord or fishing line passed over the three small pulleys K K K, the two ends of the cord being attached at equal distances on either side of the centre of the journal B. This cord is tightened up by the nut N, through the spring balance M, until the lever H floats freely. The tension on the cord, registered by M, measures the frictional moment. Thermometers, T T, register the temperature of the bearings.

Prof. Smith informs us that this machine measures the friction with extreme delicacy and accuracy, and the lever H keeps floating so long as the conditions (pressure, temperature, and lubrication) remain unchanged. The smallest variation in any one condition throws the lever on to one of its stops. The machine gives higher coefficients of friction than other methods of test have done, due to the form and arrangement of the brasses.

Let T = load on spring balance in pounds.
            r = distance between perpendiculars through centre of journal and point of attachment of cord.
            p = total pressure of brasses on journal.
            r_0 = radius of journal.
            f = coefficient of friction.

Then $$f = \frac{Tr}{Pr_0} \quad \quad \quad \quad \quad \quad (10)$$
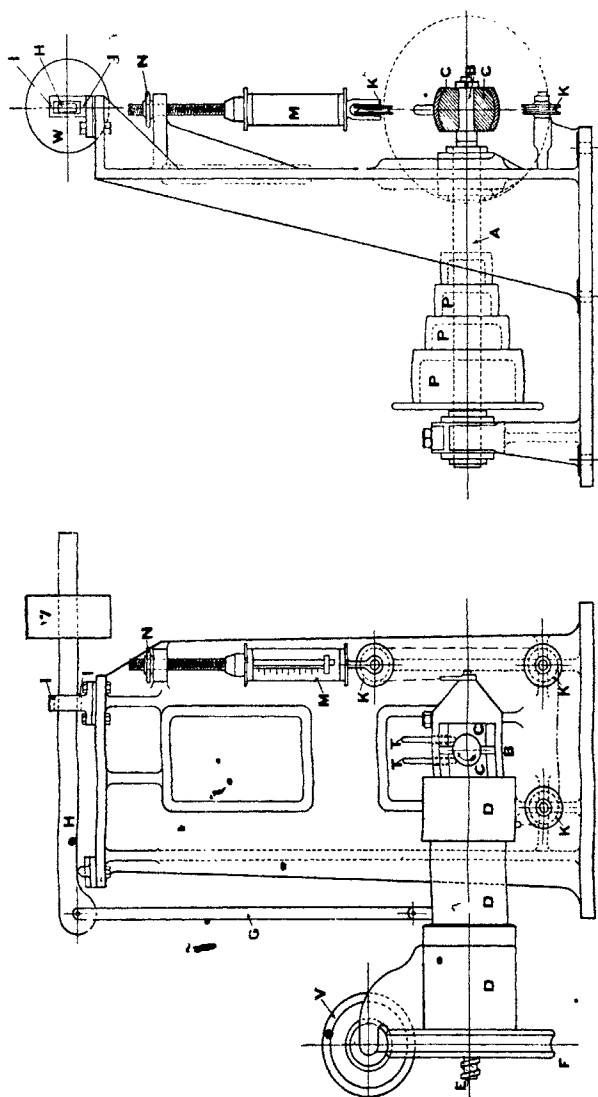
Fig. 78.

Martens' Oil-testing-Machine.—This machine, figs. 79 and 80, designed by Prof. A. Martens, has a general resemblance to Thurston's, but is modified in numerous particulars.

The hollow shaft and testing journal are provided with a water spray cooling and a steam heating arrangement, for regulating the temperature of the oil-film. The speed of the shaft is kept constant by means of a regulator. Three bronze bearings are fixed in the head of the pendulum, one on the top of the journal and the other two at distances of 120° from centre to centre on either side. The journal has an outside diameter of 100 mm. and a length of 70 mm. The bearings have a width of about 20 mm. and are pressed on to the journal by means of a Napoli hydraulic compressor screwed into the head of the pendulum, the pressure being indicated by means of a manometer. Lubrication is affected by means of an oil-bath into which the underside of the journal dips. The oil can be cooled or heated by circulating water or steam through the double walls of the bath.

A detailed description of this machine and the method of working it will be found in a report by Martens in the *Mitteilungen aus den Königlichen technischen Versuchsanstalten*, 1889, Ergänzungsheft v. pp. 12–20, and 1890, Heft i. pp. 1–8.

The machine was also fully described and illustrated in *Engineering*, 13th July 1894, to the proprietors of which journal we are indebted for the blocks from which figs. 79 and 80 are printed.

Ingham and Stapfer's Oil-testing Machine.—This tester is furnished with two brasses, one above and one below the journal. Each brass covers nearly half the circumference, and is held against the journal by a weight and lever. It is run at a speed of from 1500 to 2000 revolutions per minute. Sufficient oil having been put on to prevent the journal from becoming dry, it is run until the temperature reaches 200° F as indicated by a thermometer. The machine is then stopped and the total number of revolutions since the commencement of the test is read off from the counter. It will be seen that the conditions under which the lubricant is tested are such as to merely give the effects resulting from its viscosity. The machine is shown in fig. 81.

Ashcroft's Oil-testing Machine.—This machine is a modified form of the Ingham and Stapfer design, but has a different arrangement of levers for varying the pressure on the journal, is fitted with a dial arranged to show the frictional resistance, a counter to record the revolutions made by the journal, and a thermometer to measure the rise of temperature resulting from the heat liberated.

The journal is of rather large diameter compared with its length, and against it two brasses, each covering nearly half the circumference, are pressed by a system of levers and weights. It is manipulated in much the same way as the Ingham and Stapfer machine, and furnishes similar information. Tests for oiliness can only be properly made by cutting away the brasses, increasing the loads, and running at slow speeds.
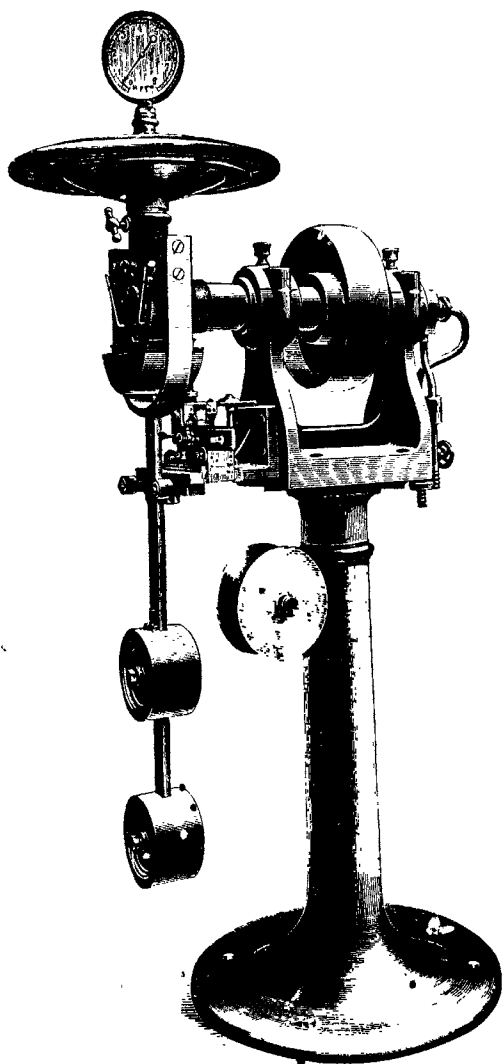
FIG. 79.—Martens' Oil-testing Machine.
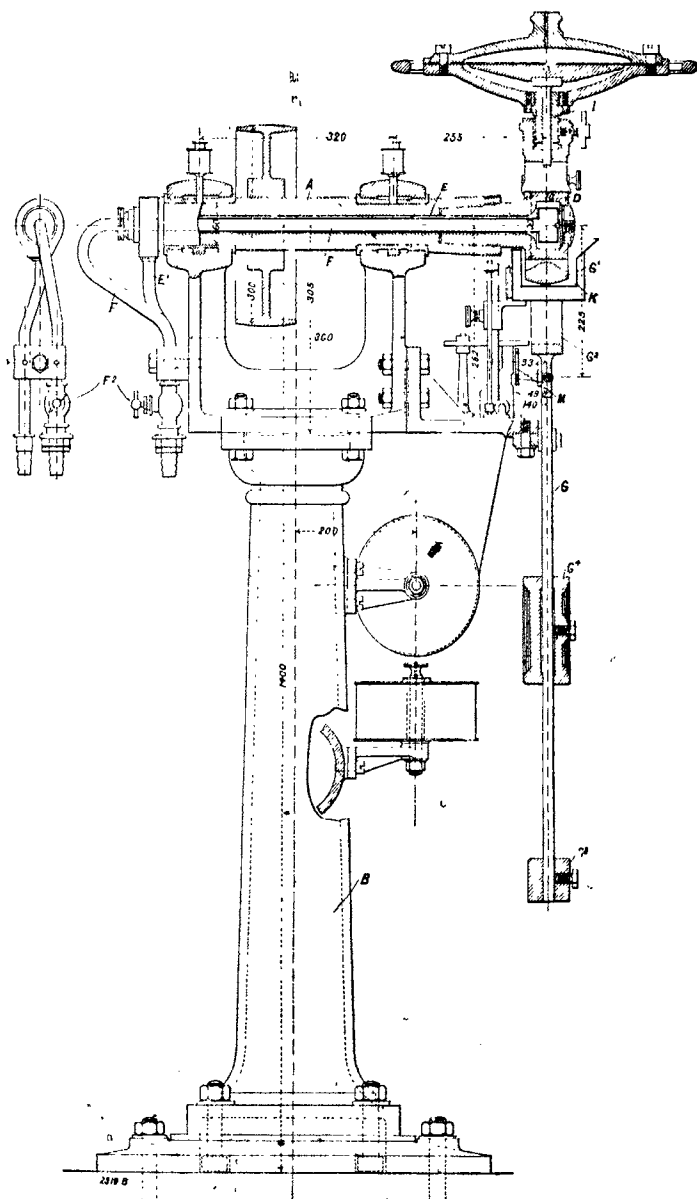
FIG. 80.—Marters' Oil-Testing Machine.

Stroudley's Oil-Testing Machine. —This machine was built so as to make the conditions of running closely resemble those of a carriage or locomotive axle. It has only one bearing, which rests upon the revolving axle A, fig. 82. The bearing carries the beam C, which has knife edges at the ends, upon which rest the suspending links and weights for applying the load.   G is a small beam and pan.

When the journal is in motion the link D is depressed, but by placing weights in the pan of the small balancing lever it is raised until the pointer P indicates that the beam is in its normal position. The weights in the pan are then a measure of the frictional resistance.   H is a small eccentric and wheel driven by a worm on the main shaft.   It keeps the brass continually moving to and fro, side play being necessary to cause the surfaces to remain free from
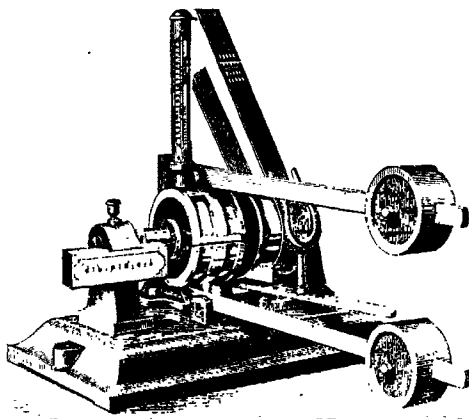
FIG. 81.

grooves.   M is an oil-pad, which keeps the journal constantly lubricated, N is a siphon lubricator, R is a revolution counter, and T a thermometer to show the temperature of the journal.

This machine, Goodman says, when accurately adjusted, runs rather more steadily than Tower's machine, consequently there is less liability to error in taking readings.   The lubricating arrangements are easily accessible, and the bottom of the shaft is quite open. Then again the load is conveniently situated, being quite free from the framing, a very important point, considering that the weights often amount to as much as 2 cwt. each.   But the disadvantage in the machine is that the most scrupulous accuracy is required in making the weights exactly equal, whilst the beam and links must also be exactly balanced.   The balancing of the weights and beam is effected as follows:—

After the beam has been machined very accurately, so that the

23

jaws into which the brasses fit are central with the knife edges on which the weights hang, a temporary knife edge is fitted in the centre of the jaws, and the beam itself balanced upon it. The links to carry the weights having been hung on and balanced, the knife edge is removed, and the brass having been fitted in is placed on a short mandril which it exactly fits. The whole is now placed on a smooth level plane, and the beam again balanced by adjusting the
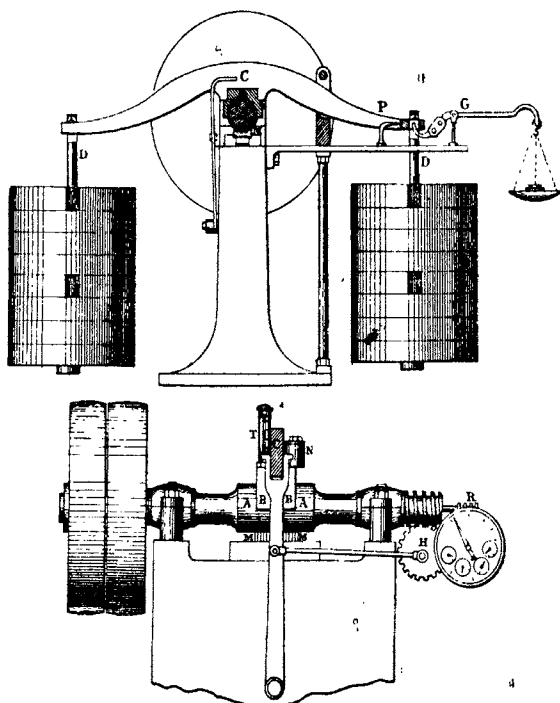
FIG. 82.

brass in the jaws until the centre of the mandril is central with the knife edges; by this means, a practically frictionless vibrating balance is obtained. The weights themselves are placed on the links, and each pair balanced and marked.

After the machine has been running for some time its balance is disturbed, unless the direction of motion has been periodically reversed. This results from the wear being chiefly confined to the 'off' side of the brass, a point to which attention has already been

alled. The inequality of wear is occasionally very rapid under heavy loads, a few days' hard running cauing the brass to wear 0·01 inch out of centre. Suppose the load to be 1 ton, or 2240 lbs., which, with an equivalent length of arm of 72 inches, gives an error of

$$\frac{0·01 \times 224}{72} = 0·311 \text{ lb.} \qquad . \qquad . \qquad . \qquad . \qquad (11)$$

in the scale pan ; this, with a 7-inch shaft, becomes an error of 0·0028 in the coefficient of friction, or an error in some instances of as much as 100 per cent. Thus, a very small error in construction, or any displacement due to uneven wear, has a serious effect upon the readings, a possibility which should never be lost sight of.

The coefficient of friction is calculated as follows :—

Let
r_0 = radius of journal.
P = weight on brass.
F = total frictional resistance.
r = length of main beam.
$\dfrac{y}{x}$ = leverage of scale beam.
W = weight in scale pan.

Then
$$\frac{Wry}{x} = Fr_0 (12) \quad \therefore F = \frac{Wry}{xr_0}. \qquad . \qquad . \qquad . \qquad (13)$$

and
$$\mu_1 = \frac{F}{P} = \frac{Wry}{Pxr_0}. \qquad . \qquad . \qquad . \qquad (14)$$

Beauchamp Tower's Experimental Testing Machine.—With this machine, a series of experiments was made on the friction of journals by a Committee of the Institution of Mechanical Engineers.[1] By using pad and bath lubrication, and running the journals at moderately-quick speeds, results were obtained which were closely in agreement with each other, and which demonstrated that under some conditions of running the friction of a journal is extremely small, and is independent of the nature of the contact surfaces. A theoretical examination by Osborne Reynolds[2] of the results obtained showed that the friction was wholly due to the viscous properties of the lubricant, and independent of the nature of the surfaces and of the oiliness or greasiness of the lubricant.

As the viscosity of a lubricant can be more satisfactorily determined by the use of a properly-constructed viscometer, and the conditions obtaining at high speeds do not give any information concerning the oiliness of the liquid used, nothing in the nature of a test of the quality of oiliness can be made with Tower's machine, unless the conditions of speed and load be such that the oil pressure-film does not form. However, as the results obtained with this machine enabled the true theory of 'perfect' lubrication to be worked out, a description of it will not be out of place.

[1] *Proc. Inst. Mech. Eng.*, 1883, p. 632.
[2] *Phil. Trans.*, 1886, p. 165.

Upon[1] the rotating journal A, fig. 83, rests a brass bearing B, held in a frame C. A knife edge, secured to this frame exactly beneath its centre, supports the weights W by means of which the load is applied. The turning moment, resulting from the friction of the journal and brass, is balanced by means of weights placed in the scale pan slung from the light iron frame D. A pointer, E, and graduated scale, indicate when the frame is in its normal position.
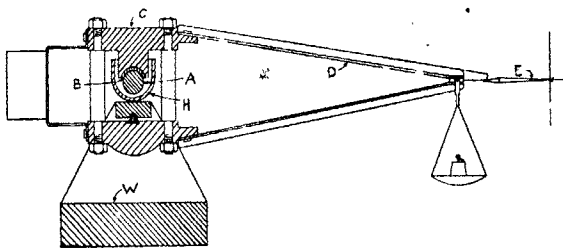
Fig. 83.

The bottom of the journal is kept well lubricated by the oil-bath H into which it dips.

When working with a weight w in the scale pan, the coefficient of friction is obtained as follows :—

$$F r_0 = w r \quad \therefore F = \frac{w r}{r_0} \qquad \qquad . \qquad . \qquad (15)$$

and

$$\mu_1 = \frac{F}{P} = \frac{w r}{P r_0} \qquad . \qquad . \qquad . \qquad (16)$$

When working with a pointer E and no scale pan, and measuring the angle θ, the centre of gravity of the weight being displaced a distance r^1 on either side of the centre of the journal, W P,

$$F r_0 = W r^1 \quad \therefore F = \frac{W r^1}{r_0} \qquad . \qquad . \qquad (17)$$

and

$$\mu_1 = \frac{F}{P} = \frac{r^1}{r_0} \qquad . \qquad . \qquad . \qquad (18)$$

Goodman's Friction-Testing Machine.—The earlier form of this machine (figs. 84 and 85) is a modification of that used by Tower, the correctness of whose experimental work has been amply confirmed by its use. A number of the experimental results obtained with it have already been given. It is thus described by Goodman:—

A is the journal on which the frictional resistance of the brass B is measured. The latter is tightly fitted into the cast-iron stirrup C, from which the weights are suspended by the link D, which rests on the knife edge E. The oil-bath, F, is filled with oil, into which the bottom of the journal dips. A lubricator, G, is provided for siphon experiments. The temperature of the journal can be kept fairly constant by using the circulating water-pipe H, the waste from

which is carried away by the pipe J. The shaft is driven by the
lathe chuck K, the revolutions of which are registered by the counter
L. The temperature of the brass is registered by the thermometer
M. The arm O carries the scale pan Q, which is suspended from
the knife edge S, the whole of which is counterbalanced by the
weight N. The pointer P, the long arm of which is balanced by the
small weight R, indicates when the arm O is horizontal.
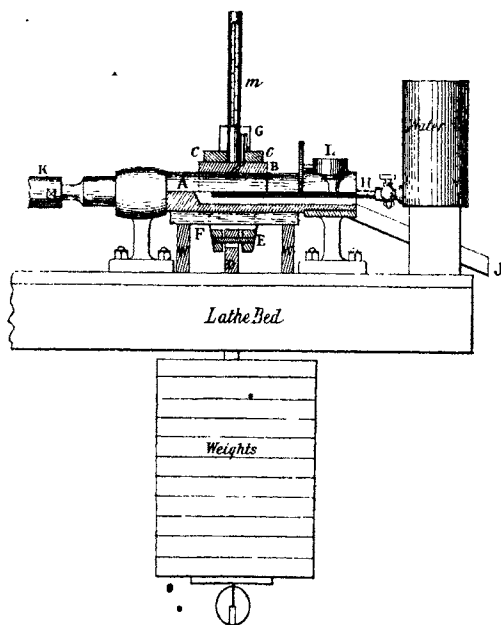
FIG. 84.

An improved form of this machine, described by Goodman in Eng.
Patent No. 22295 of 1895, is illustrated in longitudinal section
in fig. 86. The weight is suspended from the stirrup by means of
a parallel motion device, which permits the stirrup and the bearing
fixed in it to tilt or rotate through a small angle without altering the
central direction or pull of the load. The weight is applied by
means of levers, and the friction is measured by means of a floating
steelyard attached to the stirrup.

Referring to the figure, A is the test-bearing and B the axle upon
which it rests. C is the stirrup and D the floating steelyard. E
and F are a pair of connecting links of equal length, suspended from

the stirrup C by means of the knife edges G and H respectively, which are fitted in the sides of the stirrup C. The lower ends of the links E and F carry suspended from them by means of knife-edges I and J, the cross-bar K. Midway between the knife edges I and J, the cross bar K is provided with a knife edge fulcrum L, from which is suspended the central connecting link M. The lower end of the link M is connected by a knife edge N with the lever O of a compound or other lever arrangement.

It will be evident that owing to the parallel motion device formed
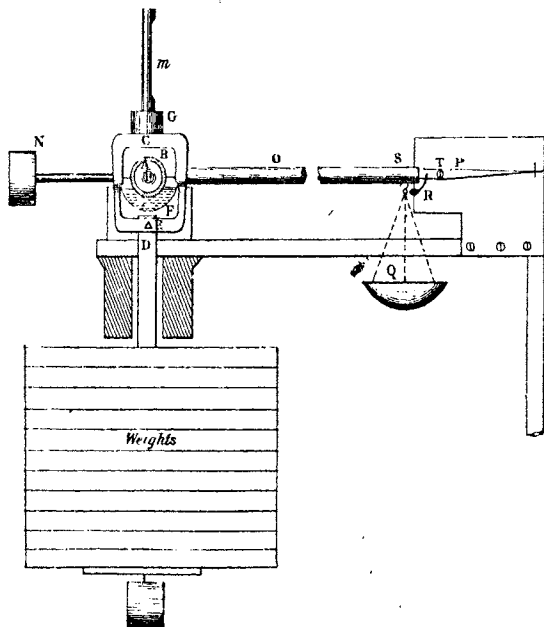
Fig. 85

by the stirrup C, crosshead or cross-bar K, and links E and F, the pull of the link M is transmitted through the centre of the axle B parallel to the links E, F, and M, whether the floating steelyard D be in a horizontal position or be tilted through a small angle by the friction between the bearing and axle.

The knife edge H is prolonged at one side, so as to be fitted with a lever P. The outer end of the lever P is provided with a hole, through which passes the screwed rod Q, the rod Q being hinged at R to the stirrup C. Two nuts, one on each side of the lever P,

fitted on the rod Q, hold the lever P firmly in position.   If the
bearing edge of the knife edge H is not a exactly the same distance
from the certie of the axle B or bearing A as the knife edge G, then
by slackening one of the said nuts and tightening up the other, the
knife edge H is tilted in one direction or the other, so as to move
the bearing edge of the same nearer to or farther away from the
centre of the axle B or bearing A, as may be required to make the
said distances exactly equal.

With this machine, Goodman has carried out an extended series
of tests of antifriction metals, ball bearings, and roller bearings.
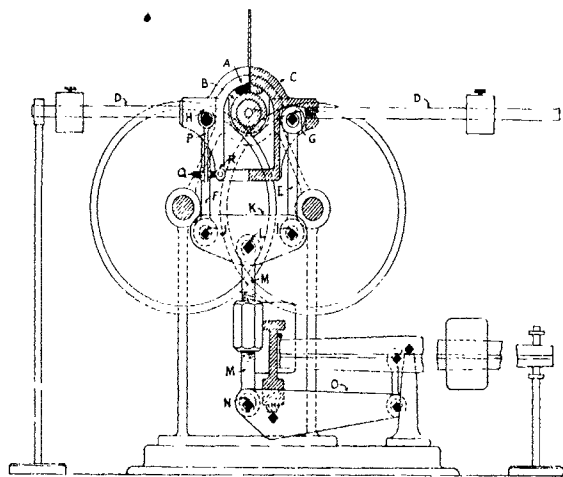
Fig. 86.

*The Riehlé U.S. 'Standard' Machine for Testing Oils and Bear-
ing Metals.* — This machine, fig. 87, is a modification of Good-
man's, and is made by his courtesy.   It can be used to test
either the wearing qualities of different bearing metals, or the
lubricating properties of various oils.   The load on the bearing is
applied by means of a turnbuckle connection between the beam and
lower lever, and is weighed on the beam by a large poise.   The
friction in pounds on the periphery of the journal is indicated by a
poise on the upper or friction beam, reading by increments of one
pound.   The journal of the machine is mounted on four large
rollers, which reduce the friction and prevent heating, which would
affect the results of temperature tests.   Ball thrust collar bearings
prevent side motion of the journal, and take any thrust in this
direction which would cause friction.

The bearing to be tested fits in a cap to which the yoke frame is
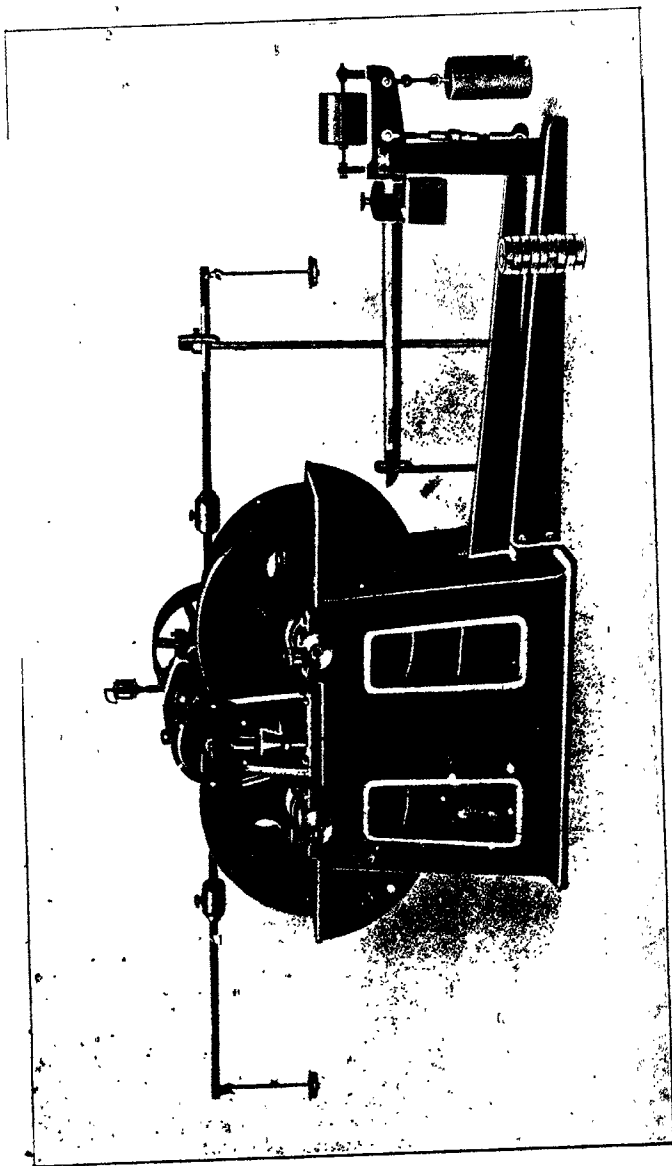
Fig. 87.—Riehlé Te

attached; this yoke frame is fitted with two knife edges equidistant from the centre of the shaft; two clevises join these knife edges with similar knife edges in the equidistant lever below, from which connection is made to the intermediate lever and the load beam. The yoke frame is thus perfectly free to rotate about the journal, and any tendency to do so will show on the friction beam. The machine is arranged to allow the pulley to drive it in either direction. The U.S. standard 'test bearing' of nine square inches projected area is used. The oil may be supplied from a sight-feed oil cup, which can be regulated; in which case it is dropped on the journal in front of the test bearing, distributes itself along the edge of it, and is carried underneath the journal; or a pad may be used, which is saturated with oil and placed in a drawer beneath the journal.

This machine is made by the Riehlé Bros. Testing Machine Co., of Philadelphia, Pa., from whose pamphlet the above description and illustration are taken.

Kingsbury's Oil-testing Machine. — Prof. A. Kingsbury has described [1] a machine and methods of testing oils designed with special reference to the conditions under which the effects due to oiliness or 'body,' on the one hand, and viscosity on the other hand, may be investigated independently. The apparatus used is also serviceable for tests under any intermediate condition. The following description is taken, by permission, from Kingsbury's paper.

Fig. 88 shows the general appearance of the testing machine, for the frame and driving parts of which a 14-inch drilling machine was utilized. The test journal has its axis vertical; it is suspended from the spindle by means of a flexible coupling and runs between two opposed bearings in a cylindrical cup or case, which may be filled with the oil to be tested if a 'bath' is desired. The load on the bearings is provided by means of a helical spring of 900 pounds capacity, with screw adjustment and with a device for quick application or removal of the load without disturbing the adjustment. This spring is enclosed in a horizontal tube attached to the side of the oil case. The cup has a cover with a small hole for the insertion of a thermometer.

The cup and attached parts are borne on a hollow vertical spindle, $1\frac{3}{4}$ inches in diameter, turning freely in a sleeve supported from the frame of the machine; the spindle extends about two feet below the sleeve, and is suspended from a fixed bracket by a tempered steel wire passing through the spindle to its lower end. In testing, these suspended parts turn freely to a position where the torsion of the suspension wire balances the friction at the test journal, and the angle of torsion, which may be as great as 270°, is read from a graduated disc. The suspended parts being counterbalanced, there is no appreciable pressure of the spindle against its sleeve; and when the oil in this bearing becomes evenly distributed, there is no error from friction, as has been amply proven by tests with an

[1] *Trans. Amer. Soc. Mech. Eng.*, vol. xxiv. (1903), 143.

'optical lever,' as well as by the uniformity of the results in use.
At the same time, the viscosity of the oil serves the purpose of
damping the oscillations which arise from variations in speed or
friction at the test journal.   This mode of suspension gives large
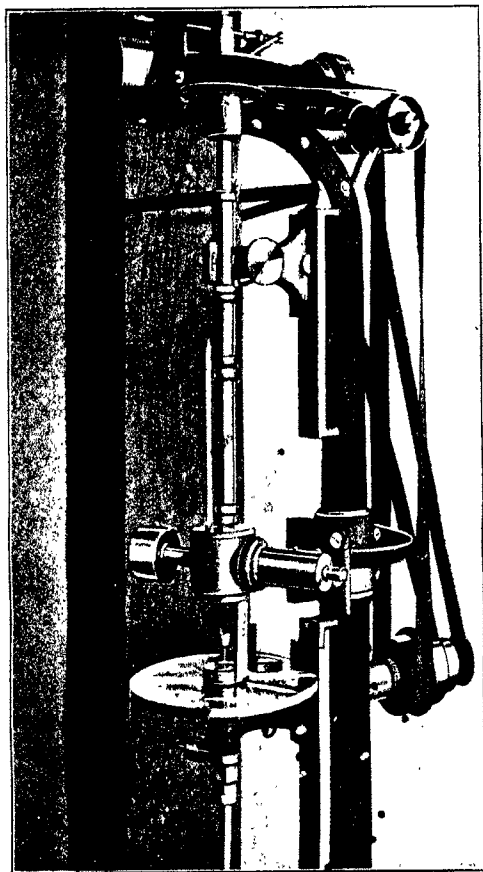
Fig. 88.—Kingsbury's Oil-testing Machine.

indications for very small frictions at the test journal, while a helical
spring placed on the extension of the spindle is added for tests
involving great friction.
    The cup and test journal contained in it may be heated as desired

by a Bunsen flame.   The revolutions of the journal are indicated by a counting device, not shown in the figure.

For tests involving perfect lubrication (friction due to viscosity only), the test journal used is $1\frac{3}{4}$ inches diameter, of tool steel, hardened, ground, and polished.   The brasses are sectors cut from a ring finished in the lathe, each having an arc of about 120° and a length of 2 inches.   These brasses are fitted with some care, so that when perfectly clean they may be made to adhere to the journal after the manner of well-fitted 'surface plates.'   In making tests, care is taken to prevent wear of these parts, which are used only under such loads that the oil film effects complete separation of the surfaces and entirely prevents wear ; the load is always relieved before starting or stopping the journal ; and, finally, a friction device in the driving coupling safeguards the journal from motion against excessive friction.   These precautions against wear are necessary to ensure the constancy of results.

For tests for comparing oils with respect to 'body' or oiliness, the best results have been obtained by the use of a hardened and polished steel journal $\frac{1}{4}$ inch in diameter, running between two brass bearings about 1 inch long : on this small journal pressures up to 8000 lbs. per square inch may be applied, if necessary.   The samples of oil to be compared are contained in small brass cups placed inside the case and surrounding the test journal, each cup having a wire for transferring oil to the journal ; the case, samples, and journal are heated together to any desired temperature.

In testing for 'body' the oils are compared in pairs, being applied alternately at the upper end of the bearing, one being applied until the friction becomes constant or nearly so ; the other is then applied until it displaces the first and the friction again becomes constant at the new value ; this process is repeated several times.   The oil giving the less friction is assumed to have the greater body.   In this way, the order of the body values of six samples of oils of the same class may generally be determined for any given temperature in an hour or less ; the friction indications rapidly follow the changes of the oils and are generally quite consistent.   When the oils to be compared are of different classes (as mineral oils with fixed oils), the first friction indications on changing oils are frequently misleading, and a longer time is required to ensure certainty of results.

The speeds for the 'body' tests are made rather low and pressures not unnecessarily high, in order to avoid heating and wear of the journal, since it is essential for comparative purposes that the surfaces should be in the same condition for both samples compared —a requisite which, above all others, led to the development of this method of testing.   Again, the actual temperature of the oil at the test surfaces is shown more nearly by the thermometer if but little heating by friction be permitted.   The order of 'body' values, as determined by this method, has been found not to vary with the speed or the pressure within a considerable range.   A speed of 50

to 100 revolutions (3 to 6 feet) per minute, with sufficient pressure to make the coefficient of friction only as great as 0·01 to 0·03, have been found most satisfactory ; the pressures being from 590 to 5000 lbs. per square inch, according to the character of the oils.

In the tests made with this machine under conditions of 'perfect' lubrication it was found that the surfaces were so perfectly separated by the oil-film that the coefficients of friction were extremely small, the minimum coefficient for all oils being found to be, approximately, 0·0006. The results obtained by different experimenters agreed remarkably well, and were found to approximately verify Reynolds' deduction from Beauchamp Tower's experiments, that the friction under conditions of perfect lubrication is proportional to the viscosity of the oil and varies, approximately, as the square root of the speed.

The 'body' or oiliness tests made with this machine are the most useful from a practical point of view, and they support the established fact that the mineral oils as a class have much less body than the animal and vegetable oils of similar or nearly the same viscosity. When, however, the difference in viscosity was great, as for instance between mineral cylinder oil and lard oil, the mineral oil was found to possess the greater body. As showing the relation between viscosity and 'body,' it is interesting to note that four cylinder oils were found to possess body in the same order as viscosity. Samples of castor, lard, olive and sperm oils also ranged themselves by the body test in the same order as that of their viscosities.

The Lahmeyer Oil-testing Machine.—This machine, shown in fig. 89, consists of a short length of shaft running in a ring-lubricated bearing, and carrying a heavy fly-wheel at each end. The shaft is provided with a pin-coupling, so that the motive power (either electrical, mechanical, or hand) can be uncoupled at any moment while running. The apparatus is supplied in four types, viz.—(a) electrically driven ; (b) mechanically driven ; (c) for hand power ; and (d) for laboratory purposes. The last is provided with fly-wheels for different bearing pressures, and an exact arrangement for measuring speed.

The method of testing is as follows :—

The bearing is supplied with the oil to be tested, the motor is started, and the fly-wheel shaft is run at full speed for a certain time. The motor is then uncoupled, and the time noted which the apparatus takes in coming to rest.

This machine chiefly measures effects due to viscosity, and it is only during the last few revolutions, when the speed is very low, that effects due to 'oiliness' will show themselves.

Disc and Collar Machines—*Suitability of, for Oil Testing.*—The wedging action of the lubricant, resulting from the different radii of the surfaces of cylindrical journals and the brasses which rest upon them, does not affect the lubrication of collar or disc-shaped surfaces to any very great extent. On this account, the loads which such flat bearings will carry are about one-eighth part of those which may

be put upon journals. Collar and disc lubrication mainly depends for
its efficiency upon the oiliness or greasiness of the lubricant used.
Such bearings would, therefore, seem to be well calculated to give good
results in oil-testing machines. Of course, they will always give com-
paratively high frictional resistances, and, therefore, must not be
regarded as suitable for comparison with those obtained with the
cylindrical bearings of actual working machines or machine tools.
However, as the conditions which obtain in lubricated bearings become
better understood, it seems likely that disc or collar machines, highly
loaded and running at moderate speeds, will be more and more ex-
tensively used for oil-testing purposes.
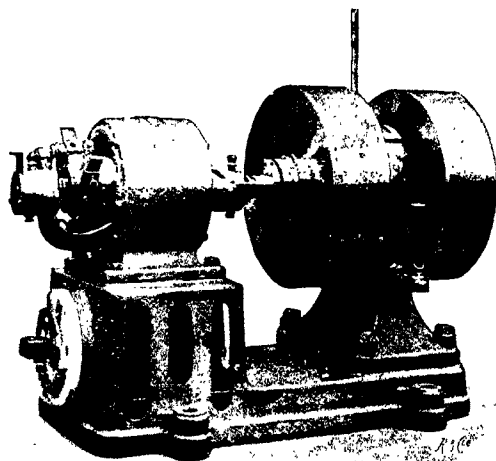
FIG. 89.

MacNaught's Testing Machine.—This, which is one of the earliest
forms of disc oil-testers, is shown in fig. 90. A vertical spindle A,
driven by a pulley D, carries on its upper end a circular plate E.
Upon this plate rests a disc F, a projecting stud, *a*, on which, when
the disc is rotated by the friction between it and the rotating plate
below, presses against a pin fixed on an arm attached at right angles
to the weighted lever G H. (This arm is not shown in the figure.)
A few drops of oil having been placed between the plate and disc,
and the apparatus set in motion, the adjustable weight J is moved
until a condition of equilibrium is established.

  Woodbury's Oil-testing Machine.—This machine is an improvement
on that of MacNaught. The lower disc is fixed to the upper end
of a vertical shaft to which the driving pulley is secured. The upper

bearing surface is an annular ring placed somewhat eccentrically with
the disc below, to secure uniform wear.   The ring is hollow, is divided
by a vertical partition into two passages through which water can
be passed to control the temperature, and the sides and top are
surrounded by a hood of hard indiarubber packed with eider-down.
The load is applied by weights placed beneath the table and slung
from a cross-bar resting upon a vertical spindle, the thrust of which is
transmitted to four points on the upper ring by a cross-shaped lever
and central ball-and-socket joint.   The bearings which carry the
upper shaft can be rotated in different directions by means of pulleys,
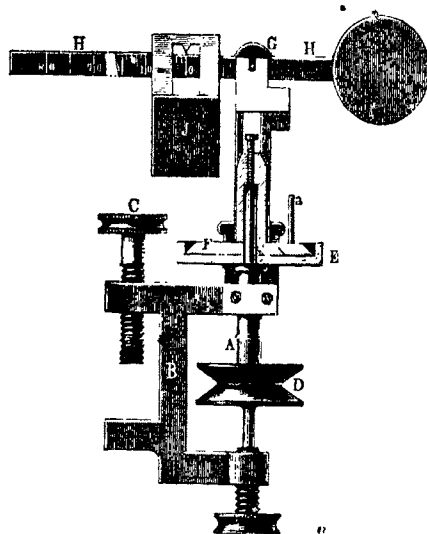
FIG. 90.

so as to reduce the frictional resistances.   This arrangement allows
the annular ring to rotate freely through several degrees and actuate
a spring dynamometer which shows the frictional resistances, the
cross-beam, weights, etc., being free to move with it.   The lubricant
under trial is conducted, by a sight-feed arrangement, through the
central opening in the upper ring to a recess in the centre of the
lower disc.   A counter indicates the number of revolutions made in
any given time, and a thermometer shows the rise of temperature.

Deprez and Napoli's Testing Machine. -This machine, which is
shown in fig. 91, resembles Woodbury's machine in some respects.
The load, which is applied by a lever and weight, forces three inclined
bronze blocks, each having a surface of 10 square centimetres, into
contact with a rotating disc below.   The turning moment is measured

by means of a pendulum, actuated by a steel band connected to the disc carrying the friction blocks S S S. An automatic record is drawn upon a sheet of paper stretched upon a small trolly set in motion by a pendulum, the pencil being fixed to a travelling arm.

Tower's Disc and Collar Oil-testing Machines. — Besides the machine for measuring the friction of journals, two other machines were designed and experimented with by Beauchamp Tower. One was for measuring disc- and the other collar-friction.
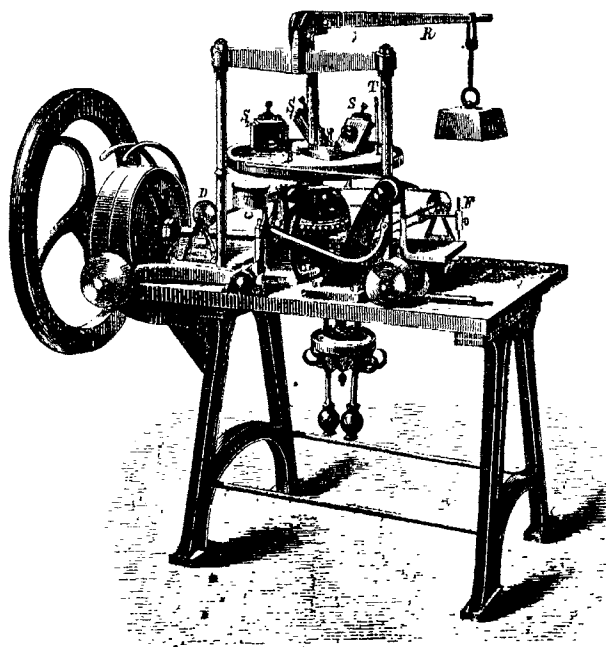
Fig. 91.

The apparatus used for measuring the friction of lubricated discs is shown in figs. 92 and 116 (p. 424). The vertical shaft carrying the footstep gears into a horizontal shaft, the driving pulley on which can be changed to give the required speeds. A hard steel centre, secured to the bottom of the bearing B, rests upon a plunger fitting the cylinder P, whilst the vertical driving shaft is fitted at its upper end with a piston T of the same diameter as that of the cylinder P. By varying the pressure of the oil, which is supplied by a hand-pump with air vessel, the pressure upon the ram can be varied so as to

give any desired load upon the contact surfaces. Two radial grooves
in the bearing, shown on a larger scale in fig. 116, pass from the
centre of the bearing face to within a short distance of its circum-
ference, and the motion causes the lubricant to flow out at its
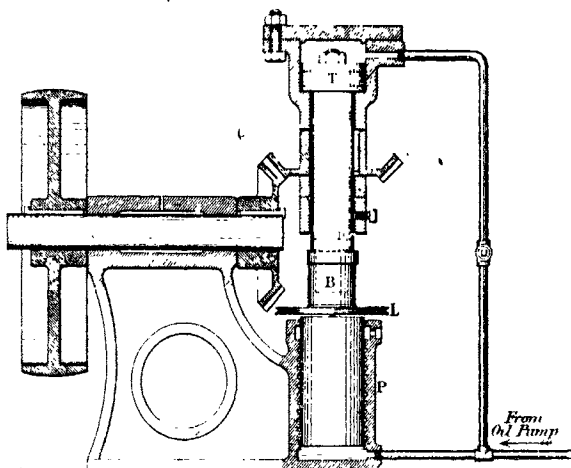
FIG. 92.

periphery into the annular space surrounding B, from which it
passes through the spout, drops into the pipe, and again enters the
bearing.   A pulley L, actuating a spring, shows the frictional
resistance of the surfaces.
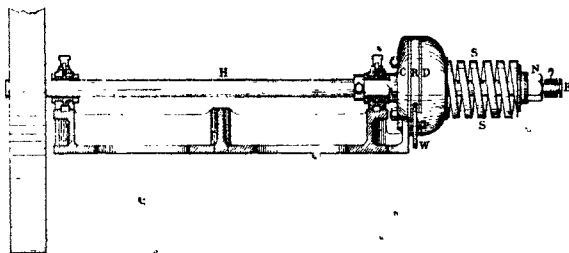
FIG. 93.

The machine shown in fig. 93 was designed to measure the friction
of a collar.   The weight was applied by a delicately adjusted spring
S, one end of which abutted against the front disc D, whilst the other
end pressed against a nut N on a central bolt B connected with the

disc C. The two discs rotating together,, and pre sing on the steel
ring R, tended by friction to carry it with them, but were prevented
from doing so by a horizontal lever attched to the ring, the friction
between the ring and discs being measured by a spring-balance
attached to the end of the lever. The methods of lubrication used,
and the conditions under which
the experiments with this machine
were made, were not such as met
with general approval, it being
considered that the information
gained by its use was not so
complete as the machine was
calculated to furnish.

Blake's Oil-testing Machine.[1]—
This apparatus consists of a
vertical shaft driven by suitable
mechanism, having a conical or
hemispherical cup on its upper
end. Into this cup is accurately
fitted a conical or hemispherical
plug which will easily revolve in
the cup, carrying a vertical spindle
or shaft to which are fitted one
or more horizontal arms to which
vanes are attached. Pressure can
be applied to the plug by means
of a weighted lever. Separate
counters give the number of
revolutions of the cup and plug
respectively. The lubricant to
be tested is placed in the cup,
and after the plug has been in-
serted, the former is caused to
rotate rapidly for a definite length
of time. The number of revolu-
tions made by the cup and plug
having been read off and recorded,
the former is cleaned and anothe.
or standard lubricant is similarly
tested. The lubricant which best
reduces the friction between the cup and the plug will cause the
latter to make the smallest number of revolutions.

Bailey's Pendulum Oil-testing Machine.—This apparatus was
designed for testing such oils as are used for watches, clocks, and
other small machines. The small brass disc linked to the pendulum
(fig. 94) rests upon a horizontal plate. When the pendulum is set in
motion, the friction of the disc slowly brings it to rest, the friction of
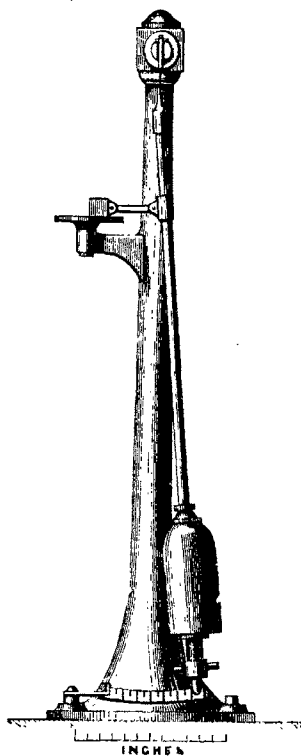
Fig. 94.

[1] Eng. Pat. 25492 of 1902.

24

the rubbing surfaces being estimated from the time required to d
this.

Friction of Screws.—The friction of screws has been exper
mentally investigated by Kingsbury [1] under the conditions of ver
slow motion, free lubrication, and pressures varying from zero t
14,000 pounds per square inch of bearing surface. The machin
used was specially designed for the purpose. The tests were mad
upon a set of square-threaded screws and nuts of the following
dimensions :—

Outside diameter of screw,	.	.	.	1·426 inch	
Inside diameter of nut,	.	.	.	1·276 „	
'Mean diameter' of thread,	.	.	.	1·352 „	
Pitch of thread,	.	.	.	.	$\frac{1}{3}$ „
Depth of nut, .	.	.	.	.	$1\frac{1}{16}$ „ (effective)

The nuts fitted the screws very loosely, so that all friction wa:
excluded, except that on the faces of the threads directly supporting
the load. The screws and nuts were flooded with the oil when place(
in the machine, which was operated by hand gearing, the screw being
driven at a very slow rate (not more than one revolution in two
minutes) until the pressure was raised to the desired amount, the
friction being measured by the swinging out of a pendulum which
carried the nut and automatically recorded on a revolving drum
The results obtained are set out in Tables XCIF to XCIJ, taken from
the author's paper.

TABLE XCIF.—MEAN COEFFICIENTS FOR HEAVY (MINERAL)
MACHINERY OIL (Sp. gr. 0·912).

(Actually read at 10,000 lbs. pressure per square inch. Each figure is the
average for eight cards.)

Screws	Nuts.			
	6 Mild Steel.	7 Wrought Iron.	8 Cast Iron.	9 Cast Brass
1. Mild steel, ...	·141	·16	·136	·136
2. Wrought iron	·139	·14	·138	·147
3. Cast iron, ...	·125	·139	·119	·171
4. Cast bronze, . . .	·124	·135	·172	·132
5. Mild steel, case-hardened, .	·133	·143	·13	·193

Mean of all, 0·1426.

Highest for a single card (screw 5, nut 9),	.	.	0·20.
Lowest „ „ (screw 3, nut 8),	.	.	0·11.

[1] *Trans. Amer. Soc. Mech. Eng.*, vol. xvii. (1896), p. 96.

XCIg.—Mean Coefficients for Lard Oil.

(Actually read at 10,000 lbs. pressure per square inch. Each figure is the average for four cards.)

Screws.	Nuts			
	6 Mild Steel.	7 Wrought Iron.	8 Cast Iron.	9 Cast Brass
1. Mild steel,	·12	·105	·10	·11
2. Wrought iron, .	·1125	·1075	·10	·12
3. Cast iron,	·10	·10	·095	·11
4. Cast bronze,	·1150	·10	·11	·1325
5. Mild steel, case-hardened,	·1175	·0975	·105	·1375

Mean of all, 0·1098.

Highest for a single card (screw 1, nut 9), . . .   0·25.
Lowest   „   „   (screw 3, nut 8), . . .   0·09.

Table XCIh.— Mean Coefficients for Heavy Machinery Oil AND Graphite.

(Actually read at 10,000 lbs. pressure per square inch. Each figure is the average for four cards.)

Screws.	Nuts.			
	6 Mild Steel.	7 Wrought Iron.	8 Cast Iron.	9 Cast Brass.
1. Mild steel,	·111	·0675	·065	·04
2. Wrought iron .	·089	·07	·075	·055
3. Cast iron,	·1075	·071	·105	·059
4. Cast bronze,	·071	·045	·011	·036
5. Mild steel, case-hardened,	·1275	·055	·07	·035

Mean of all, 0·07.

Highest for a single card (screw 5, nut 6), . .   0·15.
Lowest   „   „   (screw 5, nut 9), . .   0·03.

TABLE XCII.—MEAN COEFFICIENTS FOR HEAVY MACHINERY OIL.

(Actually read at 3000 lbs. pressure per square inch.   Each figure
is the average for four cards.)

Screws	Nuts.			
	6 Mild Steel.	7 Wrought Iron.	8 Cast Iron.	9 Cast Brass.
1. Mild steel, ...	·147	·156	·132	·127
2. Wrought iron, . . .	·15	·16	·15	·117
3. Cast iron, . . .	·15	·157	·14	·12
4. Cast bronze, ...	·127	·13	·13	·11
5. Mild steel, case-hardened, .	·155	·1775	·1675	·1325

Mean of all, 0·1433.

Highest for a single card (screw 5, nut 7), . . . 0·19.
Lowest   ,,   ,,   (screw 2, nut 9), . . . 0·11.

Kingsbury concludes from his experiments that for metallic
screws in good condition, turning at extremely slow speeds, under
any pressure up to 14,000 lbs. per square inch of bearing surface,
and freely lubricated before application of pressure, the following
coefficients of friction may be used :—

TABLE XCIJ.—COEFFICIENTS OF FRICTION.

Lubricant.	Minimum.	Maximum	Mean.
Lard oil, ...	·09	·25	·11
Heavy (mineral) machinery oil, .	·11	·19	·143
Heavy machinery oil and graphite in equal volumes, ...	·03	·15	·07

Kingsbury does not consider that the tests prove that any one of
the metals used develops less friction than any of the others, under
the methods of testing employed, although such results might be
inferred from Table XCIJ, for instance, in which the coefficients
for the brass nut are uniformly lower than for any of the others.   Nor
does he believe that the method of testing employed is the best
possible ; a number of cast-iron nuts and screws tested by themselves,
and a number of steel nuts and screws similarly tested, might give
results showing less variation than is evident in the records given
above, and hence more definitely comparable with each other.

CHAPTER X.

Forms and Functions of Friction Surfaces.—Bearings are the
surfaces of contact between the moving parts and the frame of a
machine, or of one moving part and another. They guide the motions
of the pieces they carry, and their shapes depend on the nature of
the motions required. When, for instance, the piece is required to
move in a straight line, the bearing must be either plane or cylin-
drical, with the axis in the line of motion. On the other hand,
rotating pieces must have surfaces accurately turned to figures of
revolution.

The parts of moving pieces which are in contact with the bearings
may be classified as slides, gudgeons, journals, bushes, pivots, and
screws. We also have to deal with 'line' contact surfaces which, if
they do not act as guides, yet have tangential motion.

Owing to the weight of the moving parts, or the stresses the
machine has to transmit, the bearing surfaces are pressed together
with considerable force. Consequently, not only must the moving
parts and the frame of the machine be strong enough to bear the
stresses to which they may be subjected, but the contact areas must
be sufficiently large to prevent overheating and undue wear. To
secure the required area of bearing, the rubbing surfaces are fre-
quently made very long and narrow, whilst in other instances they
are square, or approximately circular.

Materials used for Bearings and Friction Surfaces.—*Importance
of using Suitable Materials.*—Although it is true that, in the
majority of instances, the selection of a suitable lubricant, and its
proper method of application to the surfaces, are of paramount
importance, it very frequently happens that the conditions of working
are such that particular attention must be paid to the nature of the
surfaces which are to work in contact, otherwise rapid wear will
take place. Such wear may result from the fact either that the
rubbing surfaces are exposed to the atmosphere and become dirty
and gritty, or that the bearing surface is merely a line, or that the
motion is too slow or too fast and the load heavy.

373

The possibility of maintaining a machine in good condition without the frequent renewal of parts, depends largely upon the care which has been exercised in designing it so as to secure the conditions under which perfect lubrication is obtained. When the conditions are such that perfect lubrication is impossible, care must be taken to make the rubbing surfaces of as durable a material as possible. To effect these objects under the diverse conditions of everyday practice, a large number of devices have been introduced, a few of the principal of which we purpose describing.

Before the introduction of mineral oils for lubricating purposes, the necessity of paying considerable attention to the nature of the contact surfaces was not so great as now, for, as both animal and vegetable lubricants remain fairly viscous when heated, and possess the property of oiliness or greasiness very markedly, metallic surfaces, separated by fatty oils, unless subjected to excessive loads, seldom injure each other seriously. On the other hand, since the introduction of the less 'oily' mineral oils, it has been found more and more necessary to use the so-called 'antifriction metals' as bearing surfaces. Indeed, a study of the effects produced by varying the nature of the metallic or other surfaces in contact has, of late years, been forced upon the engineer by the conditions of running and the nature of the lubricants available, with the result that greater attention is now paid to this point in machine design. Of course, the advantages gained by making the bearing surfaces of different materials were recognized at a very early date: but brasses and bronzes of various kinds, working against iron or steel, proved quite sufficient, as a rule, to prevent seizing and heating.

As, when two clean surfaces work against each other, the softer of the two (providing they do not seize) wears much more rapidly than the harder one, it is well to make that surface which is most easily and cheaply replaced of the softest material. The rubbing surfaces of a bearing are, on this account, removable pieces (steps or bushes), which are easily replaced by new ones.

Indeed it is not too much to say that the introduction of mineral oils, and the recognition of the true part played by viscosity in lubrication, have necessitated great alterations in the principles of design so far as the contact surfaces of machines are concerned; for mineral oils, although stable even when heated, and giving excellent results on properly designed bearings, are generally deficient in the power of maintaining lubricating films between bearing surfaces when the speeds are low, or when the faces are pressed together by heavy loads.

In many instances, the conditions of work are such that efficient lubrication is impossible. For instance, parts of sewing machines and of watch and clock mechanism, knitting machines, and many other contrivances, such as machine gun mechanism, have to depend very largely for their durability upon the hardness of the bearing surfaces and their suitability for working in contact with each other.

Many rubbing surfaces upon which the load is small are never really lubricated, for even the contamination film is rubbed off. In such instances, it is absolutely necessary that the materials used should be exceedingly hard and such as will not adhere firmly together, even when the surfaces are chemically clean.

It is now becoming more clearly recognized that solids possess properties which have been generally regarded as peculiar to liquids. Thus lead, when quite clean, is sticky, two pieces welding together upon being brought into contact. But not only do some solids easily weld together in the cold, they even diffuse into each other.

It will be seen from this how important it is to pay the most particular attention to the physical properties of the metals used for bearing surfaces.

Hardness and its Determination.—Although we speak of bodies as being hard and soft, these are scarcely scientific terms, for the hardness of different substances measured in different ways is by no means always the same. For our purpose, hardness may be defined as the resistance offered to permanent plastic deformation. We must clearly distinguish between mere skin hardness and the hardness of the mass of the metal, for exposure to air, etc., or mechanical and chemical treatment, will often harden the surfaces of even soft bodies considerably.

A series of experiments by Bottone, who measured the load necessary to produce a cut of definite depth, show great differences in the hardness of different metals. In his scale of hardness the diamond is taken at 3010. His determinations of the relative hardness of twenty metals are as follow :—

TABLE XCII.—RELATIVE HARDNESS OF METALS.

Metal				Value	Metal				Value
Manganese,	.	.	.	1456	Gold, .	.	.	.	979
Cobalt,	.	.	.	1450	Aluminium,	.		.	821
Nickel,	.	.	.	1410	Cadmium, .	.	.	.	760
Iron,	.	.	●	1375	Magnesium,	.	.	.	726
Copper,	.	.	..	1360	Tin, .	.	.	.	651
Palladium,	.	.		1200	Lead, .	.	.	.	570
Platinum,	.	:	.	1107	Thallium, .	.	.	.	565
Zinc,	.	.	.	1077	Calcium,	.	.	.	405
Silver,	.	.	.	990	Sodium,	.	.	.	400
Iridium,	.	.	.	984	Potassium, .	.	.	.	230

Unwin has devised a method of measuring hardness by using a straight knife edge as the indenting tool. Several series of observations on the indentations produced in ⅜-inch bars of different metals with various loads were made, and for each metal a constant was deduced which is a measure of its hardness. It was found that the equation $C i = p^{1\cdot2}$ may be taken as the relation between the load and indentation, C being a constant giving the relative hardness of the metal tested, i the depth of the indentation in inches, and p the

pressure in tons per inch width of knife edge in contact with the bar.

Using this formula, Unwin obtained the following numbers expressing the relative hardness of certain metals and alloys :—

Cast steel, normal,	.	.	.	.	.	.	554·0
Brass No. 2,	.	.	.	.	.	.	216·0
Brass No. 1,	.	.	.	.	.	.	221·0
Mild steel,	.	.	.	.	.	.	143·5
Copper, unannealed,	.	.	.	.	.	.	105·2
Aluminium alloy, cast,	.	.	.	.	.	.	103·5
Copper, annealed,	.	.	.	.	.	.	62·0
Aluminium, squirted,	.	.	.	.	.	9	41·8
Zinc, cast,	.	.	.	.	.	.	40·8
Lead, cast,	.	.	.	.	.	.	4·2

The relative scales of hardness obtained by both the scratch method and the indentation method are said to be practically the same, but the scale obtained with the indentation method is a more open scale than with the scratch method, which remains to be described.

Unwin's method is not suitable for very hard or brittle bodies, or for determining surface hardness. The latter may be best ascertained by the use of Turner's sclerometer (hardness measurer), a modified form of which, described by Blount and Bloxam,[1] is shown in fig. 95.
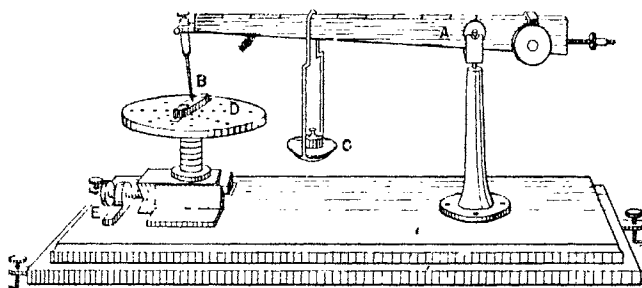
Fig. 95.—Turner's Sclerometer.

A steelyard beam A swings on a pivot in a horizontal plane and oscillates on knife edges in a vertical plane. At the end remote from the knife edge is a style B, shod with a diamond point. To prevent the style from chattering it is placed at an angle with the plane of the beam. A scale pan C slides along the beam, which is graduated, and by its means a load varying from 1 to 100 grammes can be placed upon the diamond point. The piece to be tested is prepared with a polished surface free from scratches, and is clamped on the rising table D. The diamond point is loaded with a known pressure and

[1] *Engineering Chemistry*, vol. i. pp. 28-31.

drawn across the polished clean surface. By means of the screw E the table is moved bodily a short distance—*e.g.* $\frac{1}{50}$ inch—and another trial made with a different load. The load which just suffices to abrade the specimen is a measure of its surface hardness. The instrument is preferably used in conjunction with a low-power microscope (1 inch objective) to view the scratches and decide which corresponds with the abrading load. The following table (Turner) shows the hardness of various materials, the numbers being the load in grammes required to just scratch the specimen when tested by the sclerometer:

Steatite,	.	.	.	.	.	.	.	1
Lead, commercial,	.	.	.	.	.	.	.	1
Tin,	.	.	.	.	.	.	.	2·5
Zinc, annealed,	.	.	.	.	.	.	6
Copper,	.	.	.	.	.	.	.	8
Softest iron,	.	.	.	.	.	.	15
Mild steel,	.	.	.	.	.	.	21
Tyre steel,	.	.	.	.	.	.	20-21
Hard cast iron,	.	.	.	.	.	.	36
Hardest chilled iron,	.	.	.	.	.	72

Hard Steel.—In the case of line contact, such as occurs in the various forms of trip gear for Corliss engine valves, the best results are obtained with tempered steel faces, screwed, or otherwise secured, to softer metal supports. Such faces last well if reasonable care be taken to keep them free from grit, and to lubricate them efficiently with a fairly viscous oil.

Hard steel surfaces having considerable contact areas, and carrying heavy loads, are, as a rule, made to work against softer materials. When two such hard surfaces have to work against each other, they must be very accurately fitted, and such provision made in the design as will admit of an equal distribution of the load, even if the parts should not run quite accurately together.

Low carbon steel, if used for shafting, cranks, journals, and the like, is very apt to give trouble, the metal being too soft to make good bearings. On this account, engine makers now order steel containing as much as 0·4 per cent. of carbon. With such material, every care must be taken to ensure thorough annealing at the proper temperature, otherwise large masses will prove difficult to work and be liable to fracture.

Soft steel is also very liable, when running on hard bronze bearings, especially if the lubrication becomes defective, to seize locally and pick up particles of copper, which become alloyed with the iron, and increase at every revolution by attracting fresh particles, like a rolling snowball, until at length serious heating and damage are the result.

When it is necessary to make the surfaces as hard as can be obtained by the use of very high carbon tempered steel, the speed of rubbing is generally low. There is consequently a very small liberation of heat.

Case-hardened Iron and Steel.—Hard steel is too brittle for pins,

links, and for such parts as the axles, cups, and cones of cycles. These are, therefore, made of case-hardened iron or mild steel, *i.e.* iron or steel of which the surface only has been hardened, leaving the core soft. This is effected by heating the articles to a suitable temperature (about 1000° C) in a closed box filled with finely powdered carbonaceous material such as charred leather, horn cuttings, etc., for a length of time depending upon the depth to which the carbon is required to penetrate. After cooling, the articles are reheated to about 800° C. and hardened by quenching in water. Case-hardening, unless carefully carried out, is apt to cause cracks and also to distort the mass of metal. Wrought iron and mild steel journals of large diameter are, consequently, seldom case-hardened.

Whenever very hard surfaces are made use of for bearings, it is necessary to accurately grind the case-hardened surfaces to ensure contact over the whole area.

Chilled Cast Iron. For slide-blocks and slides, chilled cast-iron surfaces, ground true, are even more suitable than those of steel or case hardened iron. Here the hardening effect is produced by casting the fluid iron into massive metal moulds or 'chills,' the sides of which are previously coated with a clay wash to prevent the casting adhering to them. In this way the cast metal is rapidly cooled, the graphite is prevented from separating from the iron, and the chilled portion of the casting becomes extremely hard, and, if broken, shows a silvery fracture. In the cooling process, however, the casting is much distorted. To remedy this, the pattern must be made of such a shape that the cooling effects shall draw the casting into the required form. To reduce the risk of fracture, it is customary to make chilled surfaces in loose pieces, which can be bolted to the frame of the machine or to its moving parts.

Cast Iron.—Excellent bearing surfaces are made of unchilled grey cast iron. The only objection that can be urged against this metal is that it is rather brittle, especially when heated by friction. It not only works well in contact with steel or wrought iron, but also against itself. Even when heated it does not seize readily, the surfaces grinding to powder and remaining free to slide over each other so long as any solid material remains. On this account it answers well for steam cylinders, in which the lubrication is apt, at times, to be very imperfect. Loose pieces are not required, for the barrel and valve faces are merely machined portions of the casting.

The suitability of cast iron for bearing surfaces arises, no doubt, in a great measure from the presence in the iron of particles of graphite, and to its porous surface, into which the lubricant insinuates itself. Sometimes powdered solids, such as plumbago, are used as lubricants for cast-iron surfaces, the powder being dusted upon the exposed portions of the rubbing surfaces.

Bronze.—In the majority of instances, the material of which a bearing is made must not only differ in melting-point and hardness from that of the surface against which it rubs, but it must also be

sufficiently strong and tough to withstand heavy blows and great stresses without fracture. Copper, although it possesses a high malleability, softness, ductility, toughness and tenacity, is not a suitable metal of which to make bearings, for it can only with difficulty be made to produce sound castings, and is too tough and close-grained to be easily shaped in a lathe. Copper is, therefore, alloyed with other metals, forming bronzes and brasses of various kinds.

The metals generally added are tin, lead, and zinc, but other elements, such as phosphorus, arsenic, antimony, bismuth, manganese, and iron, may occur as essential or accidental constituents of the alloy.

The term 'bronze' should be restricted to alloys composed chiefly of copper and tin. 'Gun-metal' is a bronze containing 90 parts of copper to 10 parts of tin. One or two per cent. of zinc, or a small amount of phosphorus, is usually added to the metal before casting, to remove oxide and promote soundness. When phosphorus is used, the alloy is known as 'phosphor bronze.' Bronzes used for bearings and friction surfaces sometimes contain as much as 18 to 20 per cent. of tin. The tin confers hardness and strength upon the alloy in proportion to the amount present; it reduces the coefficient of friction and enables a heavier load to be carried.

Lead bronzes are produced by the addition of lead to copper-tin alloys. The lead does not alloy with the copper and tin, and unless proper care be taken in casting it will separate out, but by well stirring the molten metal and by pouring it at not too high a temperature, so that it will solidify quickly in the mould, the lead remains diffused throughout the alloy and confers upon it valuable properties. Although it weakens the bronze, it greatly increases its plasticity and reduces the amount of wear. The behaviour of lead bronzes for bearings was carefully studied several years ago by Dudley,[1] who obtained the results given in Table XCIII.

TABLE XCIII.—RELATIVE WEAR OF BRONZE BEARINGS (*Dudley*).

Alloy tested	Composition					Relative Wear
	Copper	Tin	Lead.	Phosphorus.	Arsenic	
Standard lead (phosphor) bronze, .	79·70	10·00	9·50	0·80	...	1·00
Ordinary bronze,	87·50	12·50	...		...	1·49
Arsenic bronze A,	89·20	10·00	...		0·80	1·42
Arsenic bronze B,	82·20	10·00	7·00		0·80	1·15
Arsenic bronze C,	79·70	10·00	9·50		0·80	1·01
Bronze 'K,' .	77·00	10·50	12·50		...	0·92
Bronze 'B,' .	77·00	8·00	15·00		...	0·86

[1] *Jour Franklin Inst.*, 1892, pp. 81 93 and 161 172.

The method of experiment was to take a certain number of bearings made of the standard alloy, and an equal number made of the experimental alloy, and to place these on locomotive-tender or car axles in pairs, a standard and an experimental bearing being placed on opposite ends of the same axle. The relative rates of wear were ascertained by weighing the bearings at intervals. The 'ordinary bronze' not only wore half as fast again as the standard lead bronze, but a much larger percentage of the bearings made of it heated. Arsenic gave the same results as phosphorus. These elements merely promote sound castings; they were found to have no marked influence upon the rate of wear. Increasing the percentage of lead still further reduced the rate of wear, as shown by the alloys 'K' and 'B.' Bronze 'B' had a tensile strength of 10·6 tons per square inch, with 11 per cent. elongation, whilst the standard lead (phosphor) bronze had a tensile strength of 13 tons, with 6 per cent. elongation. Dudley concluded from his experiments that "the alloy which can endure the greatest amount of distortion without rupture will give the best results in wear." In other words, plasticity combined with the necessary strength is the quality to be sought after. Another desirable feature in a bearing metal is a finely granular structure, which tends to reduce the size of the particles which are torn off by the friction.

More recently, Clamer [1] has confirmed and extended the work of Dudley. He used a specially designed friction-testing machine, with test-bearings, measuring $3\frac{1}{2}$ inches $\times \frac{1}{2}$ inch, which could be readily weighed. In each experiment, the journal ($3\frac{3}{4}$ inches in diameter) made 100,000 revolutions at a speed of 525 revolutions per minute, the same pressure (1000 lbs. per square inch), oil, and method of lubrication being used throughout. It was found that the rate of wear diminished, though the friction and temperature increased, as the percentage of tin in the bronze was decreased and the percentage of lead increased (see Table XCIV.).

TABLE XCIV.—RELATIVE FRICTION AND WEAR OF LEAD BRONZE BEARINGS (*Clamer*).

	Copper.	Tin.	Lead.	Friction. lbs.	Temperature above room ° F.	Wear in Grms.
1	85·76	14·90	...	13	50	·2800
2	90·67	9·45	...	13	51	·1768
3	95·01	4·96	...	16	52	·0776
4	90·82	4·62	4·82	14	53	·0542
5	85·12	4·61	10·61	$18\frac{1}{2}$	56	·0880
6	81·27	5·17	11·14	$18\frac{1}{2}$	58	·0327
7	75?	5?	20?	$18\frac{1}{2}$	5?	·0277
8	68·71	5·24	26·67	18	58	·0204
9	64·34	4·70	31·22	18	64	·0130

[1] *Jour. Franklin Inst.*, 1903, pp. 49–77.

In order to prevent segregation of lead in the mould when casting the alloys containing more than 15 per cent. of lead, it was found necessary to keep the tin below 6 or $6\frac{1}{2}$ per cent.; and, even then, some segregation took place unless great care was taken to pour the metal at the proper temperature. The addition of $\cdot\frac{1}{2}$ to 1 per cent. of nickel, however, was found to cause more rapid solidification of the alloy, and enabled good castings to be more easily obtained.

According to recent information kindly supplied by Dudley, the alloy known as 'Ex. B metal,' which contains 15 per cent. of lead, is still used on the Pennsylvania Railway, and has proved to be a very satisfactory bearing metal. It withstands hammering nearly as well as the standard 'S' bearing metal of the Phosphor Bronze Co. The plastic bronze of the Ajax Metal Company, containing much more lead, is largely used in the United States, and has been found to give excellent results for locomotive driving-box shells, where it is well supported, and also for ordinary car bearings. It has, however, been found that the journals wear a little faster the higher the percentage of lead in the bearing metal.

Manganese bronzes, both with and without zinc, are made by introducing a proportion of ferromanganese into bronze or brass. A variety free from zinc, which has great strength and toughness, has been used for very large bearings. Great strength and toughness has also been secured by adding aluminium in small proportion.

Bronzes of various qualities are very extensively used for bearings, working both with and without lubricants. In many cases, such as where the alloy works against the bearings of cast-iron rolls, the heat resulting from excessive friction is prevented from raising the temperature unduly by a stream of water. Bronzes are also used for bearing surfaces working against steel and iron, when the load is not excessive and fluid lubricants are used, also for steam engine slide-valves working against cast-iron surfaces, especially when the load resulting from the steam pressure is great. Bronze and cast-iron surfaces are very hard and unyielding, and, unless the surfaces are very true and run accurately upon each other, they are apt to bind heavily in places and cause overheating, more especially if non-oily or non-greasy lubricants are used.

When zinc is substituted for tin, the alloy is a brass. For bearing surfaces brass is by no means so good as bronze. Nevertheless, as zinc is much cheaper than tin, and brasses are less expensive than bronzes, they are much used in cases where, owing to the load being light, strength and ductility are of secondary importance. Zinc must not be added to bronzes containing lead, as it increases the friction and also the rate of wear of the bearing.

In Table XCV. the percentage composition is given of a number of bronzes used for bearings.

The strength and efficiency of a bearing depends upon the structure of the metal it is made of quite as much as, if not more than, upon its chemical composition, and a good structure

TABLE XCV.—COMPOSITION OF BRONZES USED FOR BEARINGS.

Description.	Copper	Tin	Lead	Zinc	Other Elements.	Authority.
American Railways.						
Standard bronze ' B,' Penn Ry ,	77 0	8 0	15 0	..		Dudley
Axle-boxes and big end brasses, Chicago and N W Ry.,	85·7	14 3	...			
Eccentric strap liners, Chicago and N W Ry	78 4	5 5	11 5	4·3	...	..
English Railways						
White metalled bearings, Midland Ry ,	84 0	12 0		4 0	...	..
Plain bearings, Midland Ry.,	83 0	9 0	8 0	...	...	...
Slide-valves, Midland Ry ,	83 3	15 0	1 7	...	Phosphorus about 0 03	...
French Railways.						
Used for reciprocating parts,	84 0	14 0		2 0	...	Charpy
Journal bearings,	89 0	16 0	..	2 0	...	Ledebur.
Car bearings, Northern Ry.,	82 0	18·0	...	...	...	Ledebur and Thurston
Valve rod bearings, Orleans Ry.,	82 0	15 0		3 0	...	Charpy
Italian Railways.						
Bearing metal,	89 0	9 0	...	2·0	...	Thurston.
Miscellaneous.						
Ajax plastic bronze,	64·0	5 0	30 0	...	Nickel, 1·0	Clamer.
Ajax bronze,	81 2	11·0	7 3	...	Phosphorus or arsenic, 0·37	Dudley.
Camelia metal,	70 2	4 3	14 8	10·2	Iron, 0 5	,,
Carbon bronze,	75 5	9 7	14 6	...	Carbon, possible trace	,,
Cornish bronze,	77·8	9 6	12·4	...	...	,,
Damascus bronze,	76 4	10·6	12 5	..	...	,,
Delta metal,	92 4	2·4	5 1	...	Iron, 0 1	,,
Graney bronze,	75 8	9·2	15 1	...	...	,,
Harrington bronze,	55·7	1·0	...	42·7	Iron, 0 7	,,
Lafond's alloy, for heavily loaded bearings,	83·0	15·0	.	5 0	.	Charpy
Manganese bronze,	90·5	9·6	.	.	Manganese, nil	Dudley.
Phosphor bronze,	79·2	10·2	9 6	...	Phosphorus, 0·94	,,
Tobin bronze,	59·0	2·2	0·3	38·4	Iron, 0·1	,,

is dependent upon careful foundry practice. Job,[1] who has paid a great deal of attention to the causes of hot bearings in railway work, found that the main causes which led to heating were : (1) Segregation of the metals composing the alloy; (2) coarse crystalline structure ; and (3) dross or oxides and gas cavities in the metal.

Segregation was found to be due in many cases to an attempt to alloy the metals in improper proportions, notably to the use of excess of lead with ordinary foundry practice, resulting in liquation of part of the lead and often, also, the separation of part of the copper as

[1] *Jour. Franklin Inst.*, cxlix. (1900), pp.439-450.

'copper spots.' Pouring the metal too rapidly, at too high a tempera-
ture, is a very frequent cause of segregation and coarse crystallization,
since the metal then remains molten to o long in the mould, giving time
for alloys of different composition to crystallize out separately, tending
to produce surfaces of unequal hardness and 'heat-capacity, which
localizes friction and ultimately results in excessive heating.   A fine-
grained and practically uniform structure may be obtained, even with
a mixture of metals which do not truly alloy, by comparatively slow
pouring, so that the metal solidifies as soon as possible after it has
entered the mould, 'but not pouring too slowly, as this leads to the
formation of 'shot' in the bearing, through the freezing of the
metal before it has flowed completely into the mould.   The proper
rate of pouring must be determined by experiment.

The coarse crystalline structure often seen in defective bearings was,
in some cases, found to be due to the composition of the alloy,
antimony especially tending to produce it.   In many cases, it resulted
from rapidly pouring the metal at too high a temperature, and often
it was traced to an excess of phosphorus, silicon, or other deoxidising
agent.   A coarse structure is detrimental in two ways.   It tends to
localize friction, and secondly, by decreasing the ductility and
tensile strength of the metal, it causes an excessive rate of wear, for
it has been proven by different experimenters that, with a given
tensile strength, rapidity of wear increases with brittleness.

Another very common defect in the bearings was the presence of
dross or oxidized metal, and of large amounts of occluded gas.   The
former, by abrading the journal, causes increased friction and heating ;
the latter, by reducing the area of the bearing surface, increases the
pressure and the wear and tear.   Dross causes the metal, unless
raised too highly in temperature, to pour sluggishly in casting, and
it also prevents clean and sharp castings from being obtained.   This
sluggishness can be entirely cured by the chemical action of any good
deoxidizing material.   Thus, a small amount of phosphorus (prefer-
ably added as phosphor-copper) causes a marked increase of fluidity,
and imparts to the metal a much denser microscopical structure, as
well as greater strength and ductility.   Phosphor bronze is noted for
its fluidity, closeness of structure, strength and wearing qualities, pro-
vided it does not contain excess of phosphorus.   Excess leads to the
formation of a network of crystalline metallic salts, which increases
with repeated remelting, until finally the metal is more defective
than if no deoxidation has been attempted.   Excess of silicon leads
to similar results.

The action of zinc in producing sound castings has long been
known, but, as Dudley pointed out in 1892, the amount of zinc added
should not be more than 1 or 2 per cent.   Any excess left in the
alloy tends to cause weakness, and to decrease both tensile strength
and ductility.   In large railway foundries, 'yellow brass' is apt to
accumulate in the scrap heap, and if much of such metal be added to
the pot a considerable proportion of zinc may be introduced into the

mixture, and comparatively rapid wear result. Such yellow metal should be kept separate, and only added in just sufficient amount to each pot to introduce the requisite proportion of zinc. Zinc alone does not, however, effect complete deoxidation, and Job considers it desirable to add also a very little silicon (in the form of silicon copper) after adding the spelter or yellow metal. In this way a very close-grained and ductile metal is obtained at a moderate cost. The amount of silicon needs to be very carefully regulated, in order to avoid the partial crystallization caused by excess.

Very carefully conducted experiments made by placing bearings of practically the same composition, but differing widely both in tensile strength and ductility, upon opposite ends of the same axles, have invariably shown that increase of strength and ductility result in increased life of the bearings, confirming the observations of Dudley. An instance is given in which eight bearing brasses, each composed of copper-tin-lead mixtures, were placed under tenders of fast passenger locomotives, one bearing of each set being placed upon one end of each axle. All the bearings were practically of the same chemical composition, but one set had a tensile strength of about 16,500 lbs. per square inch, with an elongation of about 6 per cent., whilst the other set had a tensile strength of about 24,000 lbs., with an elongation of about 13 per cent., the difference being due to the fact that in the one case the metal was porous, whilst in the other it was thoroughly deoxidized, close-grained, and homogeneous. The defective set of brasses wore 35 per cent. more rapidly than the others.

In the foregoing remarks, bronzes and brasses have been considered as friction surfaces, but it is now frequently the practice to coat the surfaces of bearings with white, so-called, 'antifriction alloys,' which form the friction surface. The bronze or brass part of the bearing then becomes merely a support for the white-metal, and its composition has no influence upon the friction. Such bearing brasses can frequently be made from scrap metal, a suitable composition being :—

Copper,	.	.	.	.	.	.	.	.	.	84
Tin,	.	.	.	.	.	.	.	.	.	10
Lead,	.	.	.	.	.	.	.	.	.	2
Zinc,	.	.	.	.	.	.	.	.	.	4
									100

but the exact composition is of secondary importance, so long as the requisite strength is obtained.

White Metals.—Anti-friction, or white metals, are white alloys of tin, antimony, lead, copper, zinc, etc. It is seldom that more than three of these metals are used in any one mixture. White metals, sometimes known as white brasses, are now largely used, owing to the comparative ease with which they can be scraped down to form smooth and polished surfaces, and the satisfactory way in which by their use the friction is kept low under conditions which do not admit of perfect

lubrication This is partly owing to their plastic nature, which enables these alloys under pressure to mould themselves to the form of the journal and thus, by increasing to the maximum the area of the surfaces in contact, to distribute the load more equally over the bearing. Such bearing surfaces are also more economical than those made of bronze, for the metal removed by wear can be replaced at very small cost, and without destroying the bronze, brass, or cast-iron step of which it forms the rubbing surface.

The use of white-metal also, in many cases, enables mineral lubricants deficient in oiliness to be used in place of the more costly fixed oils. The mineral oil of Pechelbronn, for instance, was found very satisfactory when used in connection with white-metal on the Eastern Railway of France,[1] where it was tried for high-speed railway vehicles. Not only was a great pecuniary saving effected by using this oil as a lubricant in conjunction with white-metal, but the number of heated axles was reduced in the proportion of about 7 to I. At a later period[2] it was found by the same railway company that with a certain type of boxes those provided with white-metal bearings became heated thirty-seven times less frequently than those having bronze bearings. The decrease in the number of hot boxes, for the same type of boxes, resulting from the substitution of white-metal for bronze, varied from year to year, but the statistics always indicated a decided advantage in favour of white-metal. On the Paris-Lyons and Mediterranean Railway, it was found that the substitution of white-metal for bronze in the case of coal trucks, fully loaded and forming trains of 300 tons moving at a speed varying between 27 and 42 kilometres per hour, gave a diminution of friction of 20 per cent. The white-metal bearings became heated less frequently than those of bronze, and wore less rapidly.[3]

The general practice is to cast recesses in the surfaces of bearings of the ordinary form, fill them with the white alloy, and then tool and scrape the surfaces so as to fit the shafts or journals they are to work upon. Generally speaking, the bearing block or 'brass' is made of a tough bronze ; for marine work, however, cast iron is now largely used. The white-metal is let into the surface, in longitudinal or diagonal strips which stand a little 'proud' of the cast iron. This gives the shaft a chance of quickly producing a true smooth-bearing surface, which, as it wears, allows the shaft to slowly put a good face on the cast iron as well. The initial process of producing a good face should be effected under easy conditions of running, so as to avoid over-heating. Being porous, the cast-iron surface is easily contaminated by small flakes of white-metal, which, to some extent, act as lubricants. If, from any cause, a bearing of this description should become over-heated and the white-metal melted away, then the surfaces of the cast-iron ribs carry the load ; and, if the bearing be kept cool by

[1] *Revue Générale des Chemins de Fer*, April 1885, p. 216.
[2] *Bull. Internat. Commsn. Ry. Congress*, 1896.
[3] *Revue Générale des Chemins de Fer*, 1894.

directing a stream of cold water upon it, the engine need not be stopped until a favourable opportunity occurs.

To ensure the adhesion of the white-metal to the bearing, the brass, bronze or cast-iron surface must first be thoroughly cleaned and tinned. Brass and bronze bearings can be most readily cleaned by dipping or pickling for a short time in nitric acid (aqua fortis), or in a mixture of this with sulphuric acid (oil of vitrol) and water, afterwards well swilling with water to remove the acid; or the articles may be scraped and filed clean. Old bearings which need remetalling must first be boiled with caustic soda solution, or cleaned with petroleum, to remove oil and dirt. The clean and bright metallic surface must then be heated and well tinned with pure tin or white-metal, using zinc chloride ('killed spirit of salt') or sal-ammoniac as a flux, and wiping off with tow. Cast iron is best cleaned with emery cloth, after all grease has been removed, and tinned with sal-ammoniac. With a lump of sal-ammoniac and plenty of tin or white-metal, there is little difficulty in getting a well-tinned surface on cast iron, provided it is clean and free from grease.

As white metals liquefy at about 440° to 480° F., they may be melted in ordinary ladles and run directly into the recesses prepared for them, the journal or shaft side of the mould being outlined by a suitable loose iron block. As some of these alloys do not adhere very well to the walls of the recesses prepared for them, the supporting edges of the latter should be bevelled in such a way that the soft alloy is mechanically held in position.

In melting white metals they must not be overheated, as they readily oxidize on the surface, and, if hard particles of the oxide or dross thus formed become enclosed in the cast metal, the friction is increased and the bearing is very likely to run hot. Some oxidation is unavoidable, and, therefore, care must always be taken, when pouring the metal, not to allow the dross or any other foreign substance to enter the mould. When white-metal becomes dirty or pasty through being kept melted and used for some time, a small piece of rosin or tallow stirred into it will assist the dross to rise to the surface, when it may be skimmed off.

In casting antifriction alloys on to a bearing, the latter should be heated to about 200° F., and the metal should be poured at a temperature sufficiently high to keep it fluid (say 500° to 600° F. and not higher. [1] If poured too hot, or on to too hot a surface, the solidification of the alloy takes place slowly, and a coarse crystallization results, which is detrimental to cool running. Neither should the bearing on to which the metal is cast be too cold. Thus Behrens cast the same white-metal around (1) a red-hot core, (2) a hollow core cooled by running water, and (3) a core heated to 100° C (212° F.). When tested on a mandrel of polished steel revolving at high speed, the white-metal blocks cast round the red-hot and cold

[1] *Metallographist*, 1900, p. 4.

cores heated much more rapidly than the block cast round the moderately heated core. It was observed that the surface of the latter block developed, as a result of the friction, a relief pattern, due to the structure of the metal, which helped to retain the lubricant. It was also noticed that the oil became charged with minute spheroids of white-metal rubbed off the surface of the block, which were considered by Behrens to play a not unimportant part in reducing the friction.

In Table XCVI. the composition is given of a large number of white antifriction alloys which have been introduced.

As might be expected from the great variations in their composition, white metals vary greatly in the extent to which they reduce the coefficient of friction, and also in their toughness and hardness. The soft varieties when clean and working against iron or steel at exceedingly low speeds, give high coefficients of friction, but the heat produced is so small and the adhesion of the rubbing surfaces so slight that no injury is done to them. Should the pressure be locally heavy, the metal is merely flaked off, or flattened, the load relieved, and the surface burnished. On this account, white metal bearings are indispensable for certain purposes ; as, for instance, when the shaft resting on the bearing cannot be made to run quite accurately.

As an illustration of the extent to which these soft metals reduce the friction when working on hard steel at ordinary speeds without unguents, we may instance the case of Magnolia metal. R. H. Smith states that when running with pure water instead of a true unguent the coefficient is as low as 0·03, the load being about 400 lbs. per square inch. With brass, under similar conditions, the friction is five times as great.

When the pressures per square inch are great, or the bearings are subjected to severe shocks, very hard mixtures are required. Soft metals under such circumstances suffer severely, their surfaces being rubbed off in flakes.

According to Dewrance, very little lead or zinc should be contained in white metals which have to be lubricated with oils containing free fatty acids, as these acids form soaps very readily with the two metals named, and, therefore, corrode badly. Tin is not attacked so readily, and the safer plan is to use an alloy composed principally of this metal.

It will be noticed that most of the white metals given in Table XCVI., p. 388, contain antimony. This metal has the important property of preventing the mass from shrinking much upon solidification, or of actually causing it to expand and, therefore, fill the cavity in which it is run. When present in the alloy in large proportion, it makes the mixture very hard and brittle. The hardening effect is, however, generally obtained by the use of tin and zinc, toughness by copper, and softness by lead. Zinc does not alloy with lead in all proportions, and it will be found that these metals are

TABLE XCVI.—WHITE ANTIFRICTION ALLOYS.

Description	Tin.	Antimony	Lead	Copper	Zinc.	Other Elements.	Authority.
American Railways							
Bearing metal, Penn Ry,	..	13 0	87·0	...	...	...	Dudley.
Packing ring metal, Penn Ry,	˜33	˜33	83 33	...	...	...	,,
English Railways							
Bearing metal, G W Ry,	67 0	11·0	...	22 0	...	...	...
,, ,, Midland Ry,	84·2	10·5	...	5·3	...	...	.
,, ,, Taff Vale Ry,.	82 0	10 3	...	7·7	.	...	...
Dutch Railways							
Bearing metal, N & S Holland Rys,	81 5	8 8	...	9·6		..	Behrens.
French Railways							
Bearing metal,	83 1	11·4	...	5·5	...	...	Charpy.
,, ,, Orleans and W. Austrian Ry,	82 0	12 0	...	6 0	..	...	Ledebur.
Valve rod and eccentric collar bearings, Northern Ry,	82 0	10 0	...	8 0	...	...	Charpy.
Bearing metal, Western Ry,	73·0	12 0	7·0	4 0	.	Phosphor copper, 4·0	,,
Valve rod and eccentric collar bearings, P.L & M Ry.. Thurston standard white-metal,	71·0	24 0	.	5·0	...	...	,,
Bearing metal,	67·0	22·0	...	11 0	...	...	,,
Journal boxes,	42·0	16·0	42·0	.	...	..	Ledebur.
Metallic packing, Eastern Ry,	12 0	8·0	80 0	...	...	.	Charpy.
Metallic packing. Orleans and P.L & M Rys,	14·0	10 0	76·0	..	...	...	,,
Metallic packing, Northern Ry,	12·0	15 0	73 0		...	...	,,
Eccentric collar packing,	20 0	10 0	70 0	..	...	...	,,
Metallic packing, Western Ry,	32 0	3·0	60 0	5 0	...	...	,,
German Railways							
Bearing metal, Prussian Rys,	91·0	6 0	..	3 0	...	..	Behrens.
Bearing metal, Hanoverian Rys,	87 0	7·5		5 5	...	..	,,
Bearing metal, Berlin Rys,	83·0	11 0	...	6·0	...	...	Ledebur.
High-speed axles, Prussian Rys,	74·0	15 0	...	11·0	...	...	Behrens.
Russian Railways							
Car bearings,	90·0	8·0	...	2·0	...	...	Thurston.
Bearing metal,	78·5	11·5	...	10·0	..	...	,,
Swiss Railways							
Bearing metal,	80·0	10·0	...	10·0	...	...	Thurston.

TABLE XCVI. —*continued*.

Description	Tin.	Antimony.	Lead.	Copper	Zinc	Other Elements	Authority
Miscellaneous							
Antitriction metal,	98 4			1 6		Iron, trace	Dudley.
,, ,,	96 0	8 0	...	1 0			Thurston.
,, ,,	93 3	0 9	0 6	1 8		Bismuth, 0·3	
,, ,,	73 7	12 1	4 4	9 8			
Bearing metal for heavy loads,	90 0	. .	...	2 0			Horns
,, ,,	87 0	7 0	...	6 0		...	,,
Bearing metal for light loads,	85·0	10 0	...	5 0			,,
,, ,,	73 0	18 0	.	9 0			,,
Very hard bearing metal,	12 0	82 0		4 0	2 0		,,
Antifriction locomotive metal,	30 0	1·0	...	4 0	65 0	...	
Hard lead,	.	6 0	94·4	..			Dudley
Antitriction metal,	...	12 1	87 9	..			,,
Car brass lining.	..	15 4	84 9		. .		,,
Antimonial lead,		18 8	80 7				,,
Metallic packing,	33 3	0 5	64·3	...	0 15	Aluminium, 0 02, Iron, 0 01	
Babbit's antifriction metal,	88·9	7 4	...	3 7			
Caurieedale antitriction metal,	61·3	5·9	26 2	6 3	.	Graphite, nil	.
Dewrance's white-metal,	61 1	12 0	20 7	6·1			
Dewrance's locomotive metal,	33 3	44 4	..	22 2		..	Horns
Electricon antifriction metal,	5 5	19 0	75 5	...	.	..	
Fenton's antifriction metal,	14·5	..	5 5	.	80 0	..	Behrens
Glyco antifriction metal,	5 1	15 9	79 1		.	...	Dudley
Graphite bearing metal,	14 4	16 7	67 7			Graphite, nil	Horns
Hoyle's alloy for pivot bearings,	46·0	12 0	42 0				
Ibis white-metal,	11 2	11 4	77·0			...	Ledebur
Jacoby's alloy for light loads,	85 0	10 0		5 0		..	Horns
Kingston's metal,	88·0	...		6 0		Mercury 6 0	...
Magnolia metal,	5 1	14 6	79 6	...	0 5	Iron, 0 01, Bismuth, 0 44	.
Richard's white-metal,	98 5	0 1	..		...	,, 1 4	.
,, plastic metal,	77 0	12 6	1 2	9 3		..	
Salgee antifriction metal,	9 9	...	1 4	1 0	85 6	...	Dudley.
United Kingdom metallic packing,	91 5	3 0	0·9	4 8	...	.	
United States metallic packing,	89 0	4 4	0 5	6 6		...	Dudley.*
	8·33	8 33	83·33			...	Horns
Vaucher's alloy for journals,	18 0·3	2·5	1 5		75 0		
Ward's white-metal,	17 2 ·	13 4	68 7	0 4			.
Zero metal,	22·4	18 9	58 9	. .		Bismuth, 0 05	.

* New formula, used on the Pennsylvania R.R.

seldom present together in alloys. Tin, on the other hand, alloys well with both copper and zinc.

The high pressures, and, consequently, high temperatures, at which steam engines now work renders hemp, or other fibrous packing, unsuitable for piston-rod glands, for the fibre is charred by the heat and the packing loses its firmness. Metallic packings are, in consequence, largely superseding vegetable fibre. The following is an analysis of a packing which stood well in the piston-rod gland of an express locomotive :—

Lead.	Tin	Antimony	Copper
2·5	88 18	3·51	7·78

When lead is used in place of tin the alloy is too soft, and the metal is forced out of the gland in flakes.

Sometimes such alloys are placed in the stuffing-boxes, either in the form of rings or solid segments, or they are fixed as segments in special frames which are free to move laterally so that no undue pressure shall be put upon the rubbing faces if the piston rod should not run quite true. Such packings require regular and good lubrication, and the piston rods must be kept truly cylindrical, or the metal will shell out of the gland and steam will escape.

The most extensive investigations of white antifriction alloys have been made by Behrens,[1] Charpy,[2] and Baucke,[3] from whose papers the following notes are taken.

Charpy considers that bearing surfaces should be hard if a low coefficient of friction is desired, and the harder the surface the greater the load which can be carried before abrasion begins. But in practice, owing to the irregularities in bearing surfaces, contact takes place at only a small number of points, where the pressure is concentrated, and the wear and friction then become excessive. Hence a plastic metal which, under pressure, can mould itself to the form of the journal and increase the area of the surface in contact is desirable.

The results of microscopic examination show that all the antifriction alloys are composed of hard grains, embedded in a plastic alloy. The load is carried by the hard grains, which have a comparatively low coefficient of friction and do not easily cut. The plasticity of the alloy makes it possible for the bearing to adjust itself closely to the shaft, thus avoiding excessive local pressure. Such constitution may be produced in binary alloys, the hard grains being composed of a single metal such as antimony, or of a definite compound such as zinc antimonide, etc., but it is preferable to use ternary mixtures because, owing to the complex composition of the ' cement,' a constitution possessing the required qualities may be more readily obtained. The constitution of bronzes is the reverse of that of white metals. Instead of hard grains embedded in a plastic eutectic, they contain plastic crystallites of copper embedded in a hard eutectic. Bronze, therefore, has a greater tendency to cut than the antifriction alloys. When, from any cause, the film of oil becomes squeezed out from between the journal and the bearing, and the metal becomes heated, white-metal wears rapidly and may fuse, but the shaft is but little affected. In the case of bronze the portions rich in copper adhere to the shaft, as already mentioned, forming a rough surface which greatly increases the friction.

Lead and antimony do not combine. The eutectic alloy contains 13 per cent. Sb and 87 per cent. Pb, and is seen to be composed, when examined under the microscope, of very fine alternate lamellæ

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[1] *Das mikroskopische Gefuge der Metalle und Legierungen.*

[2] *Bull. Soc. d'Encouragement*, June 1898, and *Metallographist*, ii. (1899), p. 9.

[3] *Metallographist*, iii. (1900), p. 4

of lead and antimony. Other alloys contain either free lead or free antimony embedded in the eutectic alloy. The only alloys of lead and antimony which can be used in practice as antifriction metals are those containing from 15 to 25 per cent. of antimony; alloys richer in lead are too soft, and have a tendency to cut, whilst those richer in antimony become brittle and are liable to break under a heavy load.

Lead and tin do not combine. Their alloys are always composed of crystalline needles, either of lead or tin, embedded in a eutectic alloy containing about 38 per cent. Pb and 62 per cent. Sn. The maximum compressive strength is found in the eutectic alloy itself, which is the one in which the constituent metals are the most finely divided.

Antimony greatly increases the compressive strength of alloys of lead and tin. In order to avoid brittleness, the proportion of antimony in the alloy should not exceed 15 to 18 per cent., and to obtain in these conditions as high a compressive strength as possible, the alloy should contain between 15 and 90 per cent. of tin. All the ternary alloys containing at least 10 per cent. of antimony consist of hard grains, composed of a compound of antimony and tin, embedded in a eutectic alloy. These alloys, therefore, have a similar structure to the binary lead-antimony alloys, but the presence of tin as a constituent of the hard grains diminishes their hardness and also their brittleness, and, as a constituent of the eutectic alloy, increases its compressive strength. The ternary alloys are, therefore, Charpy considers, superior to the binary lead-antimony alloys as antifriction metals. The proportion of tin must exceed 10 per cent., but need not exceed 20 per cent. The antimony may vary between 10 and 18 per cent.

According to Behrens and Baucke, white antifriction alloys of tin, antimony, and copper (which always contain a large proportion of tin) are composed, morphologically, of minute malleable cuboids of $SbSn_3$, and brittle needles of $CuSn$ embedded in a matrix or ground mass composed of tin containing a percentage of copper and antimony which is greater the more rapidly the metal has been cooled. Of all the alloys examined by Charpy, the one possessing the greatest compressive strength without being brittle was composed of Sn 83·33, Sb 11·11, Cu 5·55, and Charpy considers that the best alloys should probably have such a composition within 3 or 4 per cent. The rate of cooling has a great effect on the size of the cuboids, and the compressive strength is greater the quicker the cooling.

On adding copper to lead-antimony alloys the copper is taken up by the antimony, forming the compound $SbCu_2$, which crystallizes in violet-coloured needles. The same compound also forms a part of the eutectic alloy, and the compressive strength of the metal increases. If too much copper be added, segregation takes place; the alloy then contains some drops rich in copper, having the ordinary constitution of copper-antimony alloys, in the midst of an

alloy rich in lead which solidifies later and exhibits some grains of
Sb and SbCu$_2$. From the fact that the addition of copper to alloys
containing less than 13 per cent. of Sb decreases instead of in-
creases the compressive strength, it follows that the composition of
these ternary alloys should vary only within relatively narrow limits.
By adding to alloys of lead and antimony containing from 15 to 25
per cent. Sb an amount of copper not exceeding 10 per cent., it is
possible to raise materially the compressive strength and to produce
some alloys of similar constitution to those of tin, copper and
antimony. The Chemins de fer de l'Est uses as metallic packing for
locomotive and tender bearings an alloy containing : —

Lead, ...	65
Antimony, ...	25
Copper, ...	10
	100

A few of the antifriction metals given in Table XCVI. contain zinc
as a main constituent. Some of these alloys possess a very high
compressive strength, and the tin largely neutralizes the very great
brittleness of the zinc antimony alloys. They are relatively cheap,
but difficult to prepare, owing to the oxidizability of the zinc, which
is said to be exaggerated in the presence of antimony.

Goodman, who has been engaged for several years in the inves-
tigation of antifriction alloys, discovered some time ago that the
presence of very small quantities of certain metallic 'impurities' has
a remarkable effect upon the friction.[1] The alloys in question were
composed of lead, antimony, and tin. It was found that the addition
of 0·1 per cent. of aluminium increased the friction 20 to 30 per
cent. ; on the other hand, if a similar amount of bismuth were added,
instead of aluminium, the friction was reduced. The curious observa-
tion was made that whilst 0·1 per cent. of bismuth reduced the friction
somewhat, and 0·2 per cent. reduced it still more, if 0·3 per cent.
were added the friction went up again under heavy loads ; and by a
series of experiments it was found, as shown previously by American
experimenters, that about 0·25 per cent. of bismuth gave the best
result ; from this proportion up to about 1 per cent. of bismuth the
friction immediately became much higher than it was with the best
percentage. Goodman states that he has found that if the 'impurity'
added to the alloy be a metal of smaller atomic volume than the
alloy itself, the friction goes up, and if it be a metal of larger atomic
volume, the friction goes down. As the result of long experience
and investigation, Goodman informs us that pure lead is one of
the best antifriction metals for bearings working under fairly constant
loads up to about 500 lbs. per square inch. In the friction-testing
machine illustrated on p. 359 the test journal runs in cast-iron bear-
ings lined with lead.

[1] *Third Report to the Alloys Research Committee* (1895), p 289.

Wood and Hide.— In spur and bevelled gear we have to deal with line friction. Here, one set of teeth in a pair of wheels working together is often made of some hard and dense wood, such as crabtree, hornbeam, beast or beech, fitted into an iron frame, or centre, in such a way that the teeth can be taken out and replaced with new ones when much worn. Box, beech, holly, elm, maple, oak, hickory, canewood, snakewood and lignum vitæ are also much in request for shaft bearings, etc. Of these, lignum vitæ, which will sustain very great pressures without abrasion, is, perhaps, the most valuable, more especially as it wo ks well under water. Such bearings as those of stern frame blocks and the gland in a ship's side to keep the water from entering, have this wood let into grooves cut into bushes of bronze. The strips thus let in stand somewhat above the metallic surface, so as to allow of a free circulation of water, and the grain is placed at right angles to the rubbing surface of the shaft. Lignum vitæ, also, is sometimes used for hydraulic valve faces, pivots, etc. The circumstance that it works well under water is no doubt due to the fact that throughout the cells forming the woody structure are distributed resinous substances which act as lubricants, and, however much it may be abraded, the surface of the wood has always a smaller superficial tension than has water. and, therefore, is always separated from the metal by a lubricant.

Rhinoceros hide is also largely used for gear wheels, as it wears well with small loads and runs silently.

Other Non-metallic Materials.—In the case of watches and very light, continuously running machinery, which cannot be regularly lubricated, hard steel pins running upon agate or jewelled bearings give the best results.

Even for large shafts, stone bearings are occasionally adopted. The natural stones suitable for this purpose are those which are wholly free from grittiness, and somewhat inferior in hardness to iron. Gypsum, pure clay slate, pure compact limestone, marble, and silicate of magnesia or soapstone (the last being the best) are those in most general use. Many soft rocks, such as sandstone, sandy limestones, and slates, are not suitable, as they contain crystals of quartz—a hard mineral which scratches and grinds down even the hardest steel. A non-m tallic material for bearings, called 'adamas,' consists of silicate of magnesia, ground, calcined, moulded by hydraulic pressure into blocks of suitable figures, and baked. The advantages to be gained from a lubrication point of view from the use of silicate of magnesia result from its combining a certain greasiness of surface with a degree of hardness sufficient to secure the requisite durability.

Several other mixtures of solids have been introduced which, it is claimed, run well on iron or steel without the use of any liquid lubricant whatever. They almost all contain graphite, mixed with some binding material.

At present it is only where, for some reason, oil or other lubricant is objectionable, that such antifriction materials are used; well

designed and properly lubricated surfaces having proved more reliable and economical.

A solid bearing for shafts, etc., called 'carboid,' has been introduced by Killingworth Hedges. It is said to consist of powdered carbon mixed with a certain proportion of steatite, with the twofold object of consolidating the friable carbon and decreasing the friction. The 'carboid,' which may be fixed to the rough surface of a casting by a special cement, has been used for machinery for fine fabrics which oil would injure, for the bearings of steam-heated cylinders, and also for such bearings as cannot easily be lubricated. Unwin, who determined its friction coefficient, found that it followed somewhat closely the laws of solid frictio. .

Asbestos is also largely used as an antifriction packing for taps and valves. It may be compressed until it becomes dense and hard and capable of carrying a very considerable load, yet, owing to its fibrous nature, it holds together and forms a good smooth-bearing surface.

The Lubrication of Bearings.—Before proceeding to describe the design and methods of lubrication of bearings it may be useful to give a brief summary of the main conclusions arrived at in the chapter on the 'Theory of Lubrication.'

Friction and Speed.—It was shown in Chapter IV. that both in the case of cylindrical and flat surfaces, when the speed exceeds about 10 feet per minute and the lubrication is good, the resistance offered to the relative motion of opposing surfaces, owing to the viscosity of the intervening lubricant, is approximately proportional to the square root of the speed. At lower velocities, however, the frictional resistance follows quite different laws.

Although the conditions obtaining when the load is small (10 lbs. per square inch in the case of plane surfaces and 50 lbs. when the bearing is cylindrical) are interesting from a theoretical point of view, such loads are seldom used in practice, except with very high speeds. We may, therefore, omit consideration of them here, and merely deal with such loads as have to be placed upon ordinary bearings, *i.e.* those which exceed 40 lbs. per square inch in the case of plane surfaces and 100 lbs. for journals.

When we have to deal with well lubricated surfaces and ordinary loads, the coefficient of friction of rest is slightly less, to judge by such experiments as are available, than that of very slow motion, but with increasing speed a maximum is soon reached, beyond which the coefficient of friction rapidly decreases as the speed rises, until between 10 and 100 feet per minute is reached. At about 10 feet per minute, if the lubrication be good, it should be at a minimum. Diagram fig. 24, page 60, has been drawn to show the variation of the coefficient of friction with change of speed.

Slow-speed Lubrication.—The oil-films remaining between surfaces which have been pressed together, without tangential motion, for some time, are merely superficial tension films. They are in all cases exceedingly thin. Indeed, so thin are they that the minute

irregularities of even polished surfaces are enabled to engage in each other to some extent. The greater the thickness of the surface film separating the solids, the greater the oiliness of the lubricant is said to be. A soap film, for instance, which has considerable oiliness, probably has a thickness somewhat exceeding ten millionths of a millimetre, and is stable in a humid atmosphere.

Our knowledge of the thickness of lubricating films, when they separate solid bodies, is really very incomplete; but that they are extremely thin, especially in the case of mineral oils, is proved by the fact that there is always considerable friction between even well-polished surfaces at extremely low speeds.

As, at very low speeds, the oil film is not sufficiently thick to keep the surfaces apart, they abrade each other somewhat, and when this is the normal condition of working, they must be made of metals which do not easily seize or weld together. In such cases the lowest coefficient is obtained by the use of fatty oils, which are generally mixed with mineral oils.

High-speed Lubrication.— It has been shown that when the speed of rubbing is considerable, and the load not too heavy, the manner in which the friction varies with changes of load, speed, and viscosity is such as to prove that it is then wholly due to the viscous resistance offered by the lubricant itself to motion, and is unaffected by the nature of the metals forming the rubbing surfaces.

The fact that the friction is decreased by a thickening of the lubricating film has already been fully explained. As the effect, however, is by no means self-evident, we will illustrate the case by reference to a simple experiment. A face plate is flooded with a reasonably thick oil, and upon the oil-film is placed another face plate of smaller size. At the moment the oil is inclosed, the film is a thick one, and the smaller plate may be moved about with the greatest ease. As, however, the oil is slowly pressed out from between the surfaces the resistance to motion increases rapidly, and, if the upper plate be a heavy one, the surfaces will, in a short time, close together and cause a still greater increase in the friction. From this it is clear that the thinner the oil-film the greater is the frictional resistance, and *vice versa*.

When the rubbing surfaces, whether plain or cylindrical, are maintained in constant and rapid relative motion, oil is forcibly intruded, and a film is maintained between them which reduces friction enormously. The object of the engineer should, therefore, be so to design his bearings that this film shall be as thick and have as small a viscosity as possible. When these results are obtained, the frictional resistance is very small, and the wear *nil* or nearly so.

Imperfect lubrication, we notice, results either from the fact that the speed of rubbing is very slow, that the supply of oil is restricted, or that the weight upon the bearing is too great.

When it arises from the first of these reasons, good results can only be obtained by making the surfaces that come into contact of such

materials as will not readily seize or gall each other, and by using very oily lubricants. It is, however, to an imperfect supply of the lubricant that the greatest losses by friction can generally be traced.

For many years it was the custom to put just as little oil upon a bearing as would prevent it from running hot, economy of oil being secured in the great majority of instances at the expense of the machinery and fuel. Economy in the use of lubricants is also obtained by the use of grease, but, as in the case above, with loss of power, for although greases tend to remain between the rubbing surfaces and form thick films, they are very viscous or even plastic.

However, more perfect methods of lubrication are now being introduced, and the advantages secured by their adoption are becoming more widely appreciated every day, for power users frequently keep a record of the energy exerted by their prime movers, and compare it with the energy actually consumed in doing useful work. The difference is, of course, lost in friction during transmission, and so great is this loss very often, that users of power and practical engineers are beginning to look closely into the design of bearings, etc., with a view to securing conditions favourable to a low coefficient of friction.

The sooner the fact is appreciated that not only have simple means been devised for supplying the lubricant in such a manner that the friction is reduced to a minimum, and that at the same time lubricants can be used over and over again and not wasted, the sooner the old unsatisfactory methods will disappear.

It should be clearly understood that the possibility of making practical use of such devices as will give results comparable with those obtained by Beauchamp Tower dates from the introduction of mineral oils and of non-acid fatty oils blended with them.

The original objection to *reservoir* bearings was that they required, in the first instance, a large supply of oil, which soon became viscid and useless by oxidation, etc., and that the reservoirs had to be frequently recharged.

This objection can no longer be considered valid, for good oils may now be obtained, a single charge of which can be allowed to work continuously for ten or twelve months without becoming objectionably viscid or acid.

The pressure films produced by the trapping of the lubricant when the supply is good are very considerably thicker than superficial tension films. In a particular instance, by an electrical contact method, Goodman found that a lubricating film had a thickness of one five-thousandth part (·0002) of an inch. Osborne Reynolds, from the friction of a particular bearing, estimated it to vary, in different parts, from ·00077 to ·000375 inch in thickness (·019 to ·0095 mm.). Kingsbury [1] experimented with a journal 3·82 inches in diameter and 10 inches long, bearings and journal having exactly the same radius.

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[1] *Trans. Amer. Soc. Mech. Eng.*, vol. xxiv. (1903), 143.

The chords of the bearing surfaces were 3 inches each, the speed 80 and 190 revolutions per minute, and the journal was flooded with oil. By measuring the displacement of the bearings, the oil film was found to have a mean thickness of from ·00021 to ·00023 inch under loads varying from 27 to 270 pounds per square inch. Kingsbury has reported[1] later experiments made by the Westinghouse Electric and Manufacturing Co. at East Pittsburg, in which the thickness of the oil-film was measured at different speeds up to 1200 revolutions (4710 feet) per minute. In this case the shaft was 15 inches in diameter, the bearing 40 inches in length, flooded with oil, and the total load on the bearing was 94,500 pounds. The thickness of the oil film on the 'on' side of the bearing ranged from about 0·0019 inch at 470 revolutions per minute to about 0·00314 inch at 1070 revolutions per minute. On the 'off' side of the bearing the film was found at all speeds to be thinner than on the 'on' side, as was theoretically proved by Osborne Reynolds must be the case with 'perfect' lubrication. Kingsbury states that the film thickness was probably greater than the above measurements indicated, owing to the flexure of the shaft.

In the chapter on 'The Theory of Lubrication,' the manner in which this film forms and thickens as the speed increases has been as fully considered as is possible without the introduction of advanced mathematical methods.

As previously pointed out, the importance of securing perfect lubrication has become more and more recognized since the classical experiments of Beauchamp Tower on the friction of lubricated surfaces were made. He showed that the methods of applying the lubricant to the bearing in common use are often very imperfect, and not only lead to great waste of oil, but fail to allow the bearings to make the best of what they do get.

As is almost always the case with improvements designed to give increased economy, the introduction of better designed bearings and lubricating arrangements has been comparatively slow, for, as we shall find, there are mechanical difficulties to be overcome before, in all cases, the best results can be obtained, and the improved bearings are not always the cheapest or the simplest.

Then, again, the designs of bearing in common use, and the methods of lubrication adopted, have been the result of experimental practice which did not take much note of the actual frictional resistances met with, except when they were so great that serious heating was caused. Unscientific methods have consequently been largely followed, a cheap rather than an economical bearing being aimed at.

But it is certain that in future the engineer will not be content with a bearing simply because it does not run hot and give trouble. His object, as we have said, will be to reduce the friction and wear to a minimum, and to enable the power of his motor to be

[1] *Trans. Amer. Soc. Mech. Eng.*, vol. xxvii. (1905), p. 125.

expended upon the work in hand rather than in overcoming avoidable resistances.

Even at the risk of appearing to emphasise too strongly the value of the many new designs which have been introduced for securing perfect lubrication, we shall illustrate some of the best and most largely used of them for the purpose of showing the direction in which design is now moving. In the immediate future there is every reason to expect that many improvements in detail will be introduced, and instead of the design of the rubbing surfaces of a machine and the method of application of the lubricant being regarded as of comparatively little moment, they will receive their proper share of attention by the draughtsman. Steam and other motors, etc., will then be less likely to give trouble, owing to overheated or damaged bearings, than is now the case.

In the discussion of his report on friction experiments, Beauchamp Tower said [1] it seemed to him that the important practical inference is, that it is actually possible to so lubricate a bearing that not only would metallic friction be altogether done away with, and thereby the amount of power lost by friction be reduced, but metallic wear and tear would also be abolished. He would not say that such a result was actually possible in practice now, but it was a reasonable one to aim at in mechanism. By giving a profuse lubrication, and by having the brasses so arranged that there should be a uniform pressure all over their surface, it was possible to have wear and tear between metal and oil, instead of between metal and metal.

To a reduction in the frictional resistance of the machine we must, therefore, also add the increased life of its parts secured by the adoption of more perfect systems of lubrication, and both of these advantages may, if we use proper blends of oil, be secured without increased cost or waste.

Positions for Oil-ways. —At high speeds, given a good supply of lubricant of proper quality applied at the proper place, a layer of oil becomes trapped between the rubbing surfaces and completely separates them. Upon this film rests the load. The oil, therefore, is under very considerable pressure towards the centre of the bearing surface, but as we approach the edges, the pressure falls off, and reaches zero at the margin. This is no theoretical assumption, but a fact which Beauchamp Tower discovered by perforating the brass of a journal, and connecting to the hole a pressure gauge.

As the load is completely oil-borne, the distribution of pressure in the film depends upon the direction in which the load acts. The formation of the film or pad of oil results entirely from the viscous properties of the lubricant, as also does the friction. When the speed of rubbing is slow, the lubricant is not trapped between the surfaces to any great extent, and does not form a thick sustaining film. In such cases, a lubricant possessing the property of oiliness

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[1] Second Report on Friction Experiments. *Proc. Inst. Mech. Eng.,* 1885, p. 64.

or greasiness, rather than viscosity, is necessary, fatty oils giving the best results.

The lubricant is then kept between the surfaces becau · the oil or grease films powerfully resist rupture. Oil-ways, therefore, may be cut along those parts of the faces which are being forcibly pressed together, and can be made of such lengths, and extend in such directions, that owing to the close fit of the parts they will retain the oil fed to them. This cannot, however, be done with advantage when the speed of running is high and the lubrication 'perfect,' for oil-ways cut along faces to the edges, or from holes drilled where the pressure film should be, allow the oil to escape, and the surfaces then close together.

When the lubrication is 'imperfect,' the speed of running being only moderate and the journal of large diameter, it is often very difficult to keep the bearing cool, even if fixed oils of considerable viscosity are used. In such cases, grooves, and sometimes mere flat surfaces of small width, are cut on the cylindrical surface of the journal. At other times, spiral grooves are cut round the surface of the journal, or, perhaps, several short grooves are cut at different points of the circumference. These grooves carry the lubricant between the rubbing surfaces, and the latter, therefore, are prevented from becoming dry.

C. E. Hefford,[1] R.N., has found that such a flat surface filed about 22° on the 'idle side' of the crank pin of an engine which always rotates in the same direction gives good results.

Such devices, however, except when the speeds are low, only serve to remedy the evils which result from imperfect lubrication, and should not be used in cases where the conditions are suitable for securing 'perfect' lubrication.

In the case of fixed machinery, the moving parts, in the majority of instances, rest upon the bearings, and run at speeds which admit of perfect lubrication. The lubricants in these cases can be supplied through holes and grooves cut in the cap of the bearing, for the pressure film or pad is on the lower brass. On the other hand, the axle bearings of rail way vehicles rest upon the journal, and the lubricant should be supplied at the bottom or sides. Grooves in the top brasses allow the lubricant to escape, undue wear takes place, and the bearings are liable to run hot. Vertical engine main bearings are often subject to forces which tend to lift the shaft from its seat and force it against the bottom and top brasses alternately. In this case we require a pressure film on the top as well as on the bottom brass, and no grooves should be cut in either of them. The lubricant, under such circumstances, must be applied at both sides of the bearing.

In all bearings, the oil is intruded along the 'on' side of the brass, and is expelled along the other three sides and ends. Fig. 96 shows a plan of such a surface, and the arrows indicate, roughly, the paths

[1] *The Practical Engineer*, 1st October 1897, p. 331.

of the oil across it. A portion of the oil escapes at the ends, the quantity being large when the film is thick and the lubrication good, and if some means be not advised for causing the oil thus expelled to return to the source of supply, it will be thrown about and wasted. In the majority of modern bearings guards are cast at the ends of the pedestal, and the oil, as it is thrown into them from the collars on the shaft, flows into a reservoir below the axle.

Another plan (fig. 97) for preventing the expulsion of the oil is to cut oil-ways near the ends of the bearing, and, by bevelling
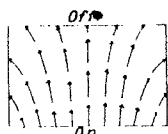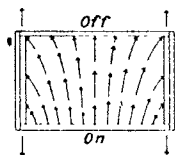
Fig. 96.   Fig. 97.

the brass, to provide channels along the edge to distribute the lubricant along the journal face. If possible, all grooves in the brasses should be avoided, for dirt is apt to collect in and fill them up.

Beauchamp Tower's experiments on the frictional resistance and loads carried by bearings with different methods of lubrication may be recounted here with advantage, as they show in a very striking manner how important it is to cut the oil-ways of bearings in proper positions. Several methods of oiling were tested by him.

When the lubricant was supplied through a hole drilled in the crown of a brass (fig. 98) which rested upon a journal, and was

Fig. 98.   Fig. 99.

distributed by means of a groove parallel to the axis of the brass and extending nearly to the ends of the bearing, it was found that the journal would not run cool when the load exceeded 100 lbs. per square inch. It appeared that the hole and groove being in the centre of pressure of the brass, allowed the supporting oil-film to escape. This view was confirmed by filling up the hole with the lubricant and then easing the weight off the journal for an instant. This allowed the oil to sink down the hole and lubricate the journal; but immediately the load was again allowed to press upon the journal, the oil rose in the hole to its former level and the journal became dry; thus showing that this arrangement of hole and groove, instead

of being a means of lubricating the journal, was a most effectual means for collecting and removing all oil from it.

In practice, greater loads are carried with this faulty system of lubrication than these experiments would seem to indicate the possibility of. This, no doubt, results from the vibrations and side-play of the axle-box on the journal, and also to the imperfect fit of the brass, which allows the oil to get out of the groove and wet the journal. When the brass is a very good fit and the oil cannot thus escape, the bearings heat and give trouble. Small grooves, however, cut from the end of the oil-way to the end of the brass will often put matters right, for the lubricant can then escape at the ends and reach the journal by a circuitous path.

As the centre of the brass was obviously the wrong place to introduce the oil, Tower resolved to apply it at the sides, where two grooves were accordingly made. They were cut parallel to the axis of the journal, as shown in fig. 99, and extended nearly to the ends of the brass. With this arrangement the bearing did not seize until the load reached 380 lbs. per square inch.

The arrangement sometimes used for locomotive axles was also

FIG. 100.
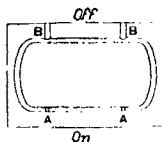
FIG. 100A.

tested. The oil was introduced through two holes, one near each end of the brass, from each of which ran a curved groove, as shown in the plan, fig. 100.

This brass refused to take its oil or run cool when the load exceeded 178 lbs. per square inch.

In many instances, such as locomotive bearings, siphon lubrication has to be mainly depended upon, it being impossible to use the same oil over and over again as in the case of some bearings shortly to be described. To retain the oil as much as possible, and prevent its expression in undue quantiti s at the ends of the journal, an oil groove may be cut as shown in fig. 100A. The lubricant is fed in by the siphon wicks through the holes A A on the 'on' side of the brass, and returns through the groove from the 'off' to the 'on' side, being thus used several times in succession. When it is possible to use an oil-pad below the axle, the two escape grooves B B may be cut. The oil raised from the pad by the rotation of the journal is then returned to the pad by escaping through these grooves; and is thus prevented from being wasted at the sides.

Pad Lubrication.—Having tested siphon lubrication with oil-ways of various kinds, Beauchamp Tower experimented with brasses which

had no oil-ways cut in them, the lubricant being supplied by pads pressed against the undersides of the journals. Although the oil was only supplied to the pads by capillary action, and the journals were only just oily to the touch, they carried loads of from 550 to 580 lbs. per square inch. The frictional resistance was also exceedingly small.

Bath or 'Perfect' Lubrication.—When the lower side of the journal dips into a bath of the lubricant, the surface is covered by a thick film of oil which is carried against the 'on' side of the brass. Under such conditions the lubrication is said to be 'perfect.' With this form of lubrication a journal has carried, without difficulty, as much as 620 lbs. per square inch.

The extent to which friction depends upon the completeness with which the exposed portion of the journal is kept wetted with the lubricant is shown in Table XV., page 83.

It is clear from these figures that improved methods of lubrication not only enable us to increase the loads on our bearings, but also to greatly decrease their frictional resistances.

The oil-bath, it appears, represents the most perfect method of self-lubrication possible, and carries us to the limit beyond which friction cannot be reduced, except by mechanical methods of oil supply. The experiments show that with speeds of from 100 to 200 feet per minute, by properly proportioning the bearing surface to the load, it is possible to reduce the frictional resistance so much that the coefficient is as low as 0·001. A coefficient of friction of 0·002 is easily obtained, and probably is often attained in engine bearings in which the direction of the force is rapidly alternating.

In the design of bearings of all kinds, the object aimed at is to secure the conditions of bath lubrication; when even these conditions will not suffice, owing to the heavy load on the brass, other means have to be adopted.

Force-Pump Lubrication.—When, owing to the loads being exceedingly great, or the speeds low, a pressure film cannot be retained automatically in the ordinary way, the best plan is to force the oil between the faces by means of a pump actuated either by the motion of the shaft itself, or by hand. Of late years this method has been adopted in quite a number of instances. Daniel Adamson states that, in one instance, a heavy shaft which gave a pressure of 2200 lbs. per square inch was kept running for years in this way without any difficulty whatever, the oil being pumped in by hand occasionally.

This method of lubrication has also been found effective for pivot bearings. Without such aid, this form of bearing surface cannot be depended upon to carry loads exceeding 100 lbs. per square inch, and to carry even these loads it is necessary to make the surfaces of suitable material and to use fatty oils of considerable viscosity. Thrust-block collar bearings might also be lubricated in this way with advantage.

Forced lubrication should also be used for high-speed motor

bearings, when the heat produced by friction cannot be carried away rapidly enough by the metallic parts and by radiation or water cooling. It should also be used where the bearing is a very close fit to the journal and practically encloses it.

Lasche's experiments show that the heat carried away by the oil supplied to a bearing is not in direct proportion to the quantity of oil, but that a small quantity of oil properly conducted between the friction surfaces and caused to circulate between them for a sufficient time to acquire a temperature approaching that of the bushes is more efficient than a larger quantity wastefully applied. In forced lubrication the oil should be applied to that part of a bearing where the frictional work or the surface pressure is greatest.

Heating of Lubricating Films.—In the chapter on solid friction it was pointed out that the work done in keeping surfaces in relative motion is transformed into heat, and that the heat produced is exactly proportional to the work done. When the surfaces are separated by an oil-film, the frictional resistance is wholly viscous, and the heat produced raises the temperature of the lubricant. This increase of temperature may be very considerable, for the film is very thin, a bad conductor of heat, and the motion of the lubricating fluid is direct. The heat produced goes, therefore, to increase the temperature of a very small volume of oil, from which, as the flow is not sinuous, the heat escapes but slowly by conduction. Osborne Reynolds calculated that even when the heating of the journal is very small indeed, and the coefficient of friction low, the temperature of the oil-film may be as much as 15° F. above that of the surrounding solid parts. In this way the fact that the friction of a journal is not proportional to the speed is explained, for the heat produced in the lubricating film decreases its viscosity.

The increase of friction with increasing speed is least marked when the lubricant is a mineral oil whose viscosity decreases rapidly with increase of temperature. W. D. Scott-Moncrieff states that in some experiments made by Napier and himself, it was found that the friction increased with an increase of velocity in the case of vegetable oils, but decreased with increasing speed with mineral oil.

When the lubrication is 'imperfect,' the loss of viscosity resulting from the heat liberated is not sufficiently great to compensate for the resulting thinner film and increased solid friction, and the frictional resistance is, therefore, greater.

The thermal units generated in a bearing per minute

$$= \frac{P\mu_1 v}{779},$$

P being the load on the bearing, μ_1 the coefficient of friction, and v the surface velocity.

The heat thus developed in the film has to be conducted through the shaft and bearing. But the quantity of heat liberated may be so great, and the lubricant, consequently, become so fluid, that it is

incapable of sustaining the load, and the rubbing surfaces, therefore, close together and may seize.

Tower's experiments clearly bring out the fact, as also do those of Goodman, that the greater the viscosity of the lubricant, the greater the load a bearing will carry, provided the speed be not too high. The seizing, when the loads are considerable, owing to the reduced viscosity brought about by increase of temperature, is somewhat more pronounced when mineral oils are used than it is with vegetable and animal lubricants, for, as previously stated, the viscosity of the latter oils does not fall off so rapidly with rise of temperature as is the case with the former. On this account mineral oils which have, at ordinary temperatures, much greater viscosity than fatty oils, can often be used without entailing increased friction.

Admissible Loads on Bearings.—The conditions which determine the area for a bearing necessary to secure cool running are very complex, and render it difficult, if not impossible, to give even an empirical rule whereby it may be calculated. Roughly, we may take it that friction always results either from actual abrasion or
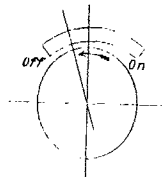
FIG. 101.   FIG. 102.

from the viscous or plastic resistance of the lubricant. When the speeds are low and the loads heavy, the more oily or greasy the lubricant, and the smaller the tendency of the surfaces in contact to gall and seize each other, the smaller the necessary contact area becomes. The lubrication of a bearing is generally so imperfect with siphon lubrication, that even up to speeds of 100 feet per minute the frictional resistance is often many times greater than that obtained with bath lubrication. At moderate or high speeds it is the viscosity of the oil which keeps the surfaces apart, for wear makes the radius of the brass somewhat larger than that of the shaft or journal, and the lubricant is trapped between them. The thickness of the film of oil is then dependent upon the form of bearing surface produced by wear, and this varies according to the conditions of running and the direction in which the load acts.

With each change of load or viscosity the relative positions of the brass and journal are also altered. With light loads, or viscous lubricants, fig. 101 shows the conditions obtaining, whilst with heavy loads, or thin oils, the relative positions of brass and journal are more nearly as in fig. 102. Increasing the load has the effect of bringing

the surfaces nearer together on the 'off' side, and causing them to part on the 'on' side. On this account, although experiment has shown that within wide limits the friction of a journal and therefore the heating effect, is independent of the load, the local heating with great pressures is greater than with small ones, although the total heat produced is, in both cases, the same. For where the film is thin, excessive heating takes place, the rate of shear being great, and, more especially when mineral oils are used, the lubricant becomes less viscous, and, when the loads are too great, allows the surfaces to actually touch and abrade each other. It will be seen that increasing the viscosity of the lubricant beyond a certain point, although it may prevent actual abrasion, does not result in decreased friction, because although the tendency is to make the film more even in thickness and prevent the surfaces from touching, more heat is liberated by the increased fluid friction of the thicker oil.

The conditions, therefore, which determine the area necessary to be given to a bearing surface are, in some measure, those which arise from the heating of the film and the nature of the metals in contact. When working under normal conditions the thickness of the lubricating film should be so great that the friction and heating cannot injure either the lubricant or the metallic surfaces; but, as it is impossible with many forms of oil supply to guarantee a proper and perfectly regular rate of feed, and also wholly to prevent the access of grit, etc., the bearing must be made large enough to carry the load, should the supply of oil be slightly insufficient.

However small the frictional resistance may be, the heat liberated must be allowed to escape from the journal and brass as quickly as possible, otherwise it will accumulate and so increase the temperature of the parts as to destroy the bearing. But, in practice, so many large masses of iron are necessarily in contact with the lubricating film, and they expose such a large surface to the air, that in the majority of cases the brasses and surfaces in contact with them, including the lubricating film, are not excessively heated, and the latter does not lose its load-carrying power to a serious extent. In the case of connecting rods and railway axle-boxes, the rapid movement through the air quickly dissipates the heat and enables comparatively heavy loads to be put upon them, even when the speeds are high.

Experimenting with a bearing the loads upon which could be varied easily, H. F. Moore[1] found that the maximum load per square inch that could be carried before the oil-film began to break down (indicated by a voltmeter in circuit between the bearing and the journal) was very closely indicated by the following formula:

$$p = 7\cdot47\sqrt{v},$$

in which

$p =$ pounds per square inch, and
$v =$ feet per minute.

[1] *American Machinist*, Sept. 24th, 1903, p. 1351.

This was with bath lubrication and ordinary machine oil. With such a bearing Beauchamp Tower found that the frictional resistance was independent of the load and proportional to the square root of the speed. It, therefore, appears that although the additional wedging action of the lubricating film, due to the increased speed, is incapable of further separating the journal and bearing, and thereby decreasing the friction, the wedging action is capable of sustaining an additional load proportional to the increased frictional resistance produced.

Although most writers on lubrication are of opinion that the area it is necessary to give the opposing surfaces of a bearing depends, in great measure, upon the heating effect resulting from the friction of the rubbing surfaces, it is admitted that a satisfactory theory cannot be based upon this consideration alone, for the sustaining power of a bearing is often increased by using a more viscous lubricant, notwithstanding the increased friction and heating the change gives rise to.

If we assume that severe heating occurs only when, owing to a deficiency in the supply of lubricant, the coefficient of friction becomes independent of the load, the results obtained by some formulæ are in agreement, to some extent, with practice; but it is certain that many bearings would heat and seize long before the lubrication became anything like so imperfect as to bring this about. However, equations based on the assumption that the area of the rubbing surfaces through which the heat is dissipated should be proportional to the heat developed by friction give some results which deserve attention.

With load W, revolutions N, radius of journal r_0, and coefficient of friction μ_1, the heat liberated by friction

$$\frac{2\pi r_0 W N \mu_1}{J} \qquad \qquad \qquad (1)$$

When the bearing completely surrounds the journal or shaft, the area of the surface through which the heat can escape from the film $= 4\pi r_0 b$ (2); one-half being the area of the brass and one-half that of the journal.

The brasses of modern journals and shafts are, however, seldom made to touch the surface which works against them over more than one-fifth or even one-tenth of the circumference. Making a the length of the brass in the direction of motion, and b its width, the area of the surface through which the heat can escape $= ab + 2\pi r_0 b$.

If H be the number of units of heat it is allowable to dissipate per unit of area in unit of time, then

$$H(ab + 2\pi r_0 b) \quad \frac{W N \mu_1 2\pi r_0}{J} \qquad \qquad (3)$$

and

$$b = \frac{W N \mu_1 2\pi r_0}{H J (a + 2\pi r_0)} \qquad \qquad (4)$$

Writing $p = \frac{W}{ab}$ we get

$$p = \frac{H J (a + 2\pi r_0)}{N \mu_1 a 2\pi r_0} \qquad \qquad (5)$$

determine the friction of cylindrical bearings. Indeed, the relative positions of the moving surfaces, even in the case of pivots and collars, vary with the direction in which the load acts, and the sustaining power of the film is thereby greatly affected. But, even when the conditions are most favourable, the load they will carry, except at low speeds, is only 60 or 70 lbs. per square inch, and even with such loads the rate of wear depends largely upon the nature of the rubbing surfaces and the quality of the lubricant.

· **Fit of Bearings.** *—Bedding of Brasses.*—Wherever possible, some end play should be given to the bearing by making it rather shorter than the neck of the journal or spindle. The faces are then free to move over each other in a direction at right angles to the circumference, and grooving and uneven wear are thereby prevented. In nearly all cases where an attempt has been made to prevent this lateral motion of the brass by making the journal smaller in the centre than at the ends, the device has had to be abandoned, circumferential grooves having been produced, and the proper formation of the oil pressure-film prevented.

When the brass is semicircular, the whole of its surface should not be allowed to come in contact with the journal. The metal should be cut away somewhat at the sides, so that the bearing area subtends an arc of 45°, or less, on each side of the line along which the load acts. This enables the lubricant to get with greater ease to that portion of the surface which has to carry the load.

Light brasses are particularly to be avoided. Not only do they leave little margin for wear, but they are apt to become distorted or fractured through the crown, just where the maximum load is carried, and where the oil pressure-film forms. When such a fracture exists, the oil escapes through it, and the carrying power of the bearing is greatly reduced. The load also pinches in the sides somewhat and destroys, for a time at least, that difference between the radius of the brass and the journal upon which efficient lubrication depends.

The harder the surfaces in contact, the more accurately should they fit one another, for it is not until the faces are everywhere brought by wear to within a few thousandths of an inch of each other that good lubrication can be secured. White metals on the other hand, are easily worked to a reasonable fit by hand, and soon wear to a perfect face.

In the case of shafts and spindles the fit should never be a tight one; enough clearance must be left for an oil-film of sufficient thickness. Some engine makers leave a clearance of 0·001 inch for each 1 inch diameter of shaft, when the diameter is not less than 1 inch or greater than 6 inches. With this clearance, the bearings will not run hot when new, and soon wear to that condition which gives the best results.

To obviate the evil effects of strains resulting from the stresses machines have to bear, long bearings should be so made as to have

freedom to move with the shaft as it deflects, otherwise the pressures are apt to become excessive at the ends.

Even when the workmanship is good, it is well to run the machine in the first instance at a moderate speed and load. This enables the bearing surfaces to bed themselves together properly and assume those curves which are the natural working ones.

Workmanship.—Owing to a want of accuracy in the fit of lathe spindles, and the spring of the centres when heavy and badly-balanced work is being turned up, it frequently happens that crank-shafts, etc., are made, the bearing surfaces of which are not truly circular. Except in rare cases, this want of trueness is sure to cause hot bearings and give endless trouble. Indeed, however well a machine may be designed, if the parts be not accurately machined and properly put together, so that the contact surfaces shall slide or rotate accurately in their bearings, not only will there be undue friction and wear, but excessive strains will be thrown on portions of the machinery, and numerous failures from overheating will be the result.

To obtain anything like the efficiency and output which a machine, such as a steam engine, may be expected to give, good workmanship is absolutely essential, for want of accuracy of fit, and defective lining up, throw upon certain portions of the engine loads which the draughtsman never calculated they would have to bear, and the effects of which the engineman finds it impossible to counteract. This does not give the machine a chance of getting into that condition in which the friction is almost wholly due to the viscosity of the lubricant, and only slightly due to the actual contact of the metallic rubbing surfaces.

Burnishing the Surfaces.—Lubricating films are so very thin that to allow of their proper formation the rubbing surfaces must be exceedingly true and smooth. To bring them into this condition before they are put to work burnishers are frequently used. The burnishing rolls are pressed firmly against the surface of the journal or other part, and produce a very excellent rubbing surface. When the material used is wrought iron, steel, or even brass or bronze, the compression of the metal causes it to flow under the burnisher and become very much harder. Indeed, the surface hardness produced may be comparable to that resulting from drawing wire through dies. Such a hard bright surface will wear much better than an annealed one, and be less liable to tear or seize.

Enclosed Bearings.—It is now becoming the practice, wherever possible, to carefully protect all rubbing surfaces by enclosing them in dust-proof cases, which shield them from grit and dirt. Too much attention cannot be paid to this point in the design of all kinds of machinery, but it is essential that the chamber in which the moving parts are placed should be fitted with openings which admit of free access to all the bearings.

Chain and spur gear, especially, should be well protected. Cycles, for example, have all such parts made as dirt- and dust-proof as

possible ; the bearing surfaces are thereby enabled to work freely on each other, and their durability is much increased.

Individual bearings, such as axle-boxes for railway vehicles, are also made dust-proof ; for now that oils which will not seriously gum or become acid can be obtained, lubricants may be used over and over again, provided they are kept free from dust and dirt.

There are numerous instances in which rubbing surfaces cannot easily be protected from air, water, dust, etc., and in which the lubrication cannot but be imperfect. As a rule when this is the case, neither of the surfaces is made of a soft material, as grit, etc., may become imbedded in the surfaces of the metal and act as cutting tools. Various hard substances are brought into requisition for such purposes ; for the load to be carried, the speed of rubbing, and the presence or absence of jars or knocks, have all to be taken into account when selecting a suitable material. In some cases toughness, as well as hardness, is of importance, whilst in other cases a hard but comparatively brittle material will give the best results.
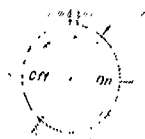
Fig. 103.
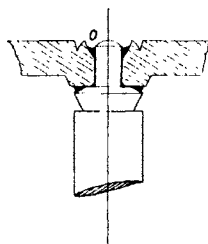
Fig. 104.

Cylindrical Bearings. — *Bush Bearings.* — Light axles, spindles, etc., are usually supported by bearings which completely surround their rubbing surfaces. Such bearings are either plain bushes threaded over the spindle, or are composed of two portions which form an upper and a lower brass. As the weight is on the bottom brass, the lubricant is supplied through an oil-hole drilled in the top cap, and is spread over the bearing by a longitudinal groove. When the shaft is a moderately good fit, the results obtained by this simple form of bearing are excellent, for, as will be seen from fig. 103 (which is not drawn to scale), the annular space between the shaft and bush will, if the gap be not too large, be maintained full of oil by capillary forces, and the conditions of working will approach those of bath lubrication.

· When the load is considerable, the oil-film becomes thin at the point of nearest approach on the " off ' side, the lubricant escapes at the ends, does not properly fill the gap between the upper brass and the journal, and the lubrication becomes imperfect. The increase of

friction thus brought about may be seen when the upper brasses of the main spindle-bearing of a foot lathe are removed. The friction will then, be found to have increased greatly, for the oil fails to properly reach the 'on' side, and the bearing surfaces approach each other somewhat closely.

Watch and Clock Bearings.[1]—As bearings of this kind have often to run for years without attention, they should be constructed so as to retain, by the action of capillary forces, a small amount of oil. The bearing of a watch or clock pivot is shown in fig. 104. The oil sink O is deep and narrow, and holds a considerable charge of oil, which is prevented from spreading by the sharp angle formed by the edge of the surrounding groove. A portion of the shoulder is also bevelled to form a narrow recess in which oil can be stored. The back taper on the spindle below the collar, and also the boss on the plate, are to prevent, as much as possible, the oil from spreading.

Means for retaining a supply of oil are also provided when the
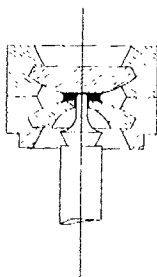
Fig. 105.
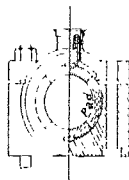
Fig. 106.

pivots run in capped jewels. Such a bearing is shown in fig. 105. Here the charge of oil is retained by capillary forces between the two jewels, which approach each other closely. One of these is perforated for the pivot, and the other is flattened to steady it laterally.

Pedestals.—The bearings or steps used for the support of shafts of any size are, as a rule, loose pieces of metal held in position by iron pedestals. When the load to be carried is very great, the pedestal is placed upon a sole-plate, which serves to distribute the load over a sufficiently large area of masonry. It also serves as a means of adjustment. In some cases, however, separate bearing pieces are dispensed with, the step then becomes a portion of the pedestal. When this is the case, to enable any wear to be taken up, and also to facilitate the removal and fixing of the shaft, the pedestal is fitted with a cap secured in position by bolts and

[1] *Friction, Lubrication and Lubricants, in Horology,* by W. T. Lewis, pp. 43–59.

projections. By reducing the thickness of the packing pieces which are placed between the cap and the pedestal, any slackness resulting from vertical wear can be taken up. Such a simple design is only suitable in cases where the speed and load are small. At one time the lubricant was nearly always supplied through a hole ·in the centre of the cap, and distributed along the surface of the shaft by two grooves which extended to within a short distance from the edges of the bearing.

The difference between the diameter of the shaft and that of its bearing being very small, the lubricant, even if a liquid one, remains between the surfaces in virtue of the play of surface forces. For line shafting and the main bearings of engines, up n which the load is often very considerable, the pedestals are always so designed that bearings or steps can be replaced with new ones when much worn.

Even now many very primitive designs are in use, which not only cause needless waste of oil, but also of power, for the friction coefficient is much larger than it should be. The shaft, in the cases alluded to, runs upon a bronze bearing, and to prevent the lubricant running off at the sides, and being wasted, the latter is only supplied in small quantities. The proper lubricating pad or film is consequently unable to form, and the faces are always, to some extent, abrading each other. On this account, pure mineral oils deficient in greasiness give but poor results when used for such bearings.

An improved pedestal, shown in fig. 106 (p. 411), is now being very extensively used. Only a short arc of the cap and brass are in contact, or nearly so, with the shaft, the spaces at the sides being occupied by felt pads kept moistened with oil from a siphon lubricator. With this arrangement, the frictional losses are comparatively small. Better bearings even than these are now being brought into use. They are so contrived that the lubricant is thrown over the shaft is a continuous stream, forms a thick lubricating film, and is again returned to the bearing after passing into a reservoir below. Under these conditions the lubrication is perfect, *i.e.* viscosity has free play, and mineral oils, with a slight admixture of fatty oils, answer admirably, if the surfaces be of the proper materials.

In such bearings the lubricant is in continuous circulation, the same charge often lasting for nearly twelve months.

Fig. 107 shows such a bearing, made by the Brush Engineering Co., Ltd., Loughborough. Here the pedestal forms an oil reservoir from which the lubricant is raised by means of an endless chain slung upon the shaft, by which it is kept in motion. The lower part of the chain dips into the oil-bath and carries up with it a thick film of oil, which is distributed over the top of the shaft through the longitudinal oil-ways. To prevent the oil being thrown about and thus wasted when it is expressed at the ends of the bearing, splashers are cast at the ends of the pedestals, to collect and return the oil to the reservoir.

Some care is necessary in selecting the material of which to make the oil-lifting chains, for the lubricant is apt to become somewhat acid with age. Iron, steel, or brass, used alone, work well, but on no account should two varieties of brass or steel be used together, one for the pins and another for the links, as they set up electro-chemical action, which destroys them.
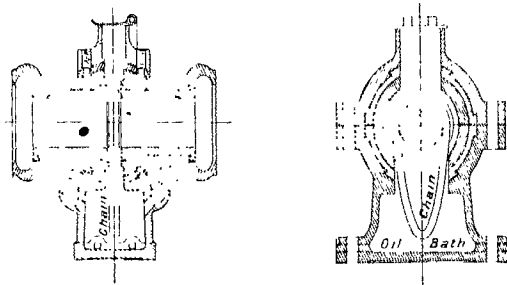
FIG. 107.

In this design the bearing is a long one, suitable for a high-speed dynamo or motor shaft. The brasses and their cast-iron supports are held in position by a ball-and-socket arrangement, which allows them perfect freedom to adjust themselves so as not, under any conditions, to throw awkward strains upon the brasses.
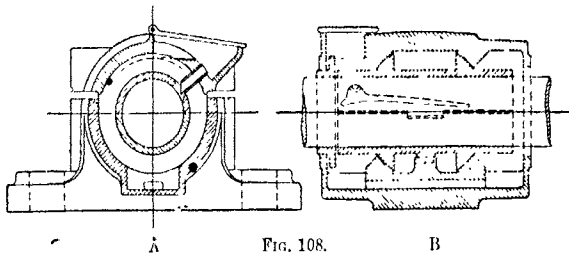
FIG. 108.   B

A self-adjusting bearing which has some good features has been designed by G. F. Thompson. The construction of the bearing is shown in fig. 108, A and B. The step, as will be seen, is supported on ring-shaped bearings or collars which are turned so that the surfaces by which they rest on the plummer-blocks are portions of a sphere. The lubrication is effected by an oiling collar, revolving with the shaft and dropping into the oil-well below; the oil adhering to this collar is scraped off, as the latter revolves, by a spring scraper at the top, and flows thence into an upper oil well, from which it passes by oil-ways to the journal.

In the bearing made by Thomas Parker, Limited, Wolverhampton, shown in fig. 109, the oil is lifted from the reservoir by means of a loose ring threaded on to the shaft. In other cases a loose collar takes the place of the chain or ring, whilst some makers of bearings place a felt pad along the top of the upper brass, to act as a strainer for the oil. The pedestal casting in such cases forms a splasher projecting beyond the bearing, and serves to collect the oil thrown out at the ends and return it to the reservoir. When the speed is very great, the oil is liable to be thrown off the ring or collar, instead of reaching the bearing.

Lasche points out that ring lubrication for high-speed motor bearings should only be used when the heat produced by the friction can be sufficiently carried away by the metallic parts and by radia-
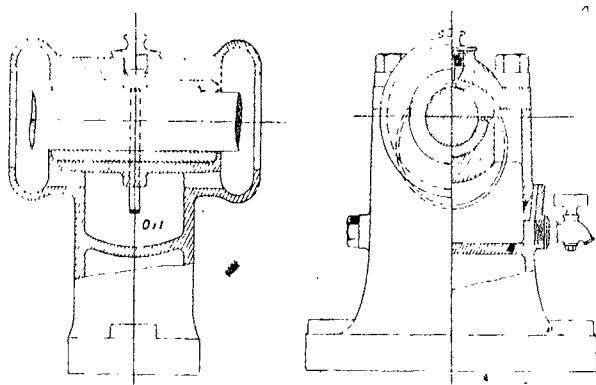
Fig. 109.

tion or water cooling. In other cases, forced lubrication (see p. 402) should be employed.

When the shaft is heavy, it is well to make the lower brass rest in a cylindrical seating concentric with the shaft, and to prevent it from rotating by suitably shaping the bearing surfaces of the brass in the cap. This enables the lower brass to be removed by merely turning it round when the shaft has been lifted only a fraction of an inch.

In some instances, the direction in which the load acts is not by any means a vertical one, owing to the strain of a belt or some other lateral force. The dividing line between the brasses should then be at right angles to the direction of the resultant pressure on the journal, and, therefore, not horizontal.

The practice of making the brasses in three or more pieces is sometimes resorted to, as it enables the wear to be taken up without removing the bearing pieces. In many cases, however, the division

between the separate pieces alloys the lubricant to escape just where the maximum pressure of the supporting film should be, whilst in all such cases the sustaining power is reduced and the friction coefficient increased. When there is only one brass the shaft can move into that position which has been shown to give the lowest coefficient of friction; but when the bearing consists of two or more separate pieces of metal, each bearing piece must be free to move somewhat and adjust itself so as to occupy its proper position with regard to the shaft, and each 'on' edge must be properly lubricated. When such adjustments cannot freely take place and the load is considerable, the bearings give a high coefficient of friction and easily run hot.

For high speeds it has been found advisable to make the bearings of large area, and cast iron is then often used, for the loads per square inch in such cases are small. The longer the bearings, the more necessary does it become to construct them as shown in figs. 107 and 108, so that no undue strain shall be thrown upon their ends if the shafting should be bent or somewhat out of line.

Many high-speed bearings are now not only fitted with two rings or chains slung on the axle and rotating with it so as to pick up the oil, but they have also small oil-pumps, driven by a cam on the axle, which deliver the oil on to the bearing in a constant stream. Such extreme precautions against the possibility of a failure in the proper supply of the lubricant are by no means unwarranted, for they ensure a low coefficient of friction, and almost wholly prevent wear of the bearing surfaces.

Axle boxes for Oil.— In the case of the bearings of railway vehicles, the brass or step rests upon the journal, and the load acts vertically downwards. The journal usually projects beyond the wheel, and can be enclosed in a dust-proof box fitted with a door at the front to enable the condition of the journal to be ascertained at any moment. But on some locomotive engine bearings, the axle-box is placed inside the wheels, and cannot be designed on quite the same lines as railway coach bearings.

Locomotive driving and trailing bearings are of bronze lined with white-metal, the lubricant being supplied by siphons fixed above them. in some instances an oil reservoir is placed in the axle-box keep, and a lubricating pad fixed therein, so as to press against the under-side of the axle.

The method of cutting oil-ways along the centre of the bearings and making it a good fit at the sides, which, in the case of driving wheel bearings, is considered to be the best practice, is not always followed in the case of other locomotive engine bearings, for the driving axle has to carry the thrust of the piston as well as the vertical load. The groove, by, to some extent, preventing the pressure film from forming, causes the crown of the bearing to wear more rapidly than it otherwise would do, and tends to prevent the side thrust of the connecting rod from developing side play. The trailing wheel bearing, on the other hand, is cut away at the sides, the arc of contact being

about 90°, so as to give the oil free access from the pad to the crown of the bearing. The single groove along the crown is also sometimes replaced by oil-ways which enclose the area over which the pressure film should form. Locomotive engine axle-boxes which are placed inside the wheels, and are not fitted with a door to enable the pad to be easily got at and cleaned, have auxiliary siphon lubrication appliances. Provision must be made in many cases to take the thrust due to the brake blocks by massing the arc of contact of bearings and axle of sufficient width. Locomotive bearings lined with good white-metal, and having an oil-way across the centre of the brass, will carry 275 lbs. per square inch, the width of the step being calculated on an arc of about 90°.

The most satisfactory tender and bogie axle-boxes are constructed upon the lines of those used for the coaching stock, drawings of some of which will now be given.

For railway vehicles which have brake blocks on both sides of the
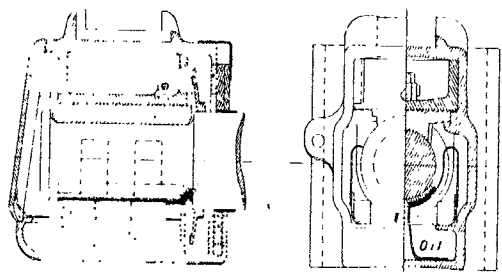
Fig. 110.

wheel, and are, therefore, only subject to slight lateral pressure, the best practice is to make the arc of contact short, the brass long in a direction parallel with the shaft, and to supply the lubricant by means of a pad pressed against the under-side of the journal.

An axle-box of this kind is shown in fig. 110. Here, the lower portion of the box forms a reservoir for the oil, into which thick cotton wicks hang from the pad. The oil rises in the capillary pores and keeps the pad and journal well moistened. The brass is a loose piece which, by lifting the box a short distance from the axle, can be taken out and examined when the door at the front is open. No oil grooves or holes of any kind are cut in the face of this brass, as they would more or less prevent the pressure-film from forming properly. To prevent the oil from escaping from the box, and to keep out dust and dirt, the door is made a good fit, whilst on the inside the axle is grasped by wooden shutters sliding in grooves. All the oil expressed at the inside edge of the brass passes into the small auxiliary reservoir, and is picked up by the disc fixed to the axle and transferred to the bearing by a wiper.

Owing to the fac that these boxes are kept cool by being brought into contact with the open air, and that there is a good deal of vibration and variation in the direction and intensity of the pressure between the surfaces, the bearings can be made to carry heavier loads than can stationary bearings of similar design, running at equally high speeds.

In this country it is the custom to make the steps of bronze, and to lubricate with mixed oils. It would seem, however, that when the bronze is replaced by a suitable white metal, pure mineral oils can be used and a great saving effected in the cost of the lubricant. The customary load put upon bearings of high-speed vehicles is about 250 lbs. per square inch. Boxes of this description, when used for locomotives and their tenders, work most satisfactorily when the spring rests upon an independent plate interposed between it and the axle-box. This plate is so guided that the axle-box may move
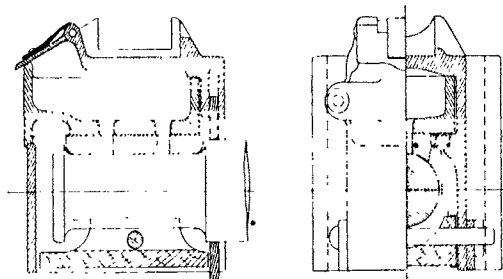
Fig. 111.

independently of the spring and thus prevent irregular strains being placed upon the bearing.

Grease Boxes.—A fluid lubricant is only, as a rule, used for the axle-boxes of quickly-moving vehicles; for wagons, grease is often preferred, the frictional resistance at starting being smaller with plastic lubricants than with fluid ones.

A grease box, Ellis' patent, such as is used on mineral wagons, is shown in fig. 111. In some respects it resembles the box used for oil, but differs from it in the important particular that the lubricant is supplied through large holes near the ends of the bearing, the melting point of the grease being such that if the bearing becomes a little warm the grease becomes fluid, and finds its way upon the journal.

Spindle Bearings.—Parsons has introduced a very ingenious bearing for shaft running at such extremely high speeds as 9000 revolutions per minute. It is impossible to balance such quick-running shafts so accurately that the centre of gyration shall coincide with the centre line of the journal. To prevent undue

pressure being put upon the bearing, and also the vibration which would result from making the shaft a somewhat loose fit, the inventor threads upon the shaft—one upon the other—several bushes, the outside one of which fits the pedestal casting. Between each bush oil-films form, which, by their viscosity, damp out all vibrations. All the bushes need not be free to rotate. These bearings are often used for the shaft of Parson's turbo-motor when the speed is high, the oil being supplied continuously to the bearing by means of a pump, which keeps up a constant circulation of oil.
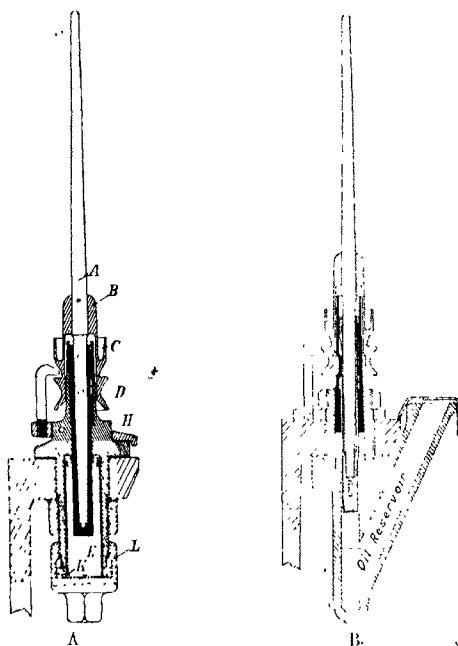
Fig. 112 —Ring Spindle.

The bearing surfaces of moderately high-speed spindles are nearly always coned, so that any wear can be taken up by moving the pedestal or spindle laterally, and the surfaces upon which the spindles run are often made of white-metal. The best spindles are obtained by shaping them from hard rolled bars of steel, the metal, in this state, being flexible and of very even texture.

The ring spindles used in textile mills for spinning the finer counts of cotton and silk run in a bath of thin mineral oil, which enables speeds of 10,000 revolutions per minute to be attained. Fig. 112A shows the construction of a ring spindle of the 'flexible'

type manufactured by Messrs. Platt Bros. & Co. of Oldham. The steel spindle A, to which are firmly attached the sleeve B, the cup C, which holds the bobbin, and the wharve D, which receives the driving band, rotates in a perforated tube or bolster E, in the bolster-holder H, which is fixed to the rail of the spinning frame. The brass oil-tube K, containing sufficient oil to nearly fill it when in position, is inserted into the bolster-holder from below and secured by means of the cast-iron nut, L, and a leather washer. The oil entering the tubular bolster through the perforations keeps the spindle perfectly lubricated. The detachable oil tube enables the dirty oil to be emptied out and the tubes to be replenished with clean oil whilst the spindles are running, and without risk of soiling the yarn, bobbin, or rings. This only requires doing once every three or four months.

Another pattern of ring spindle, manufactured by the same firm, is shown in fig. 112B. In this type of spindle the lubricant is supplied through a front oil spout, which also can be filled or emptied as the spindle runs.

Loose Pulleys.—Loose pulleys, as a rule, are merely bushed with bronze, and run upon accurately turned shafts, their lateral motion being prevented by the fixed pulley on one side and a collar on the other. Sometimes such pulleys are only supplied with a drop of oil occasionally ; in other instances they have screwed into them a small oil-cup which feeds very slowly.

Smith's self-oiling pulley is shown in fig. 113. The boss of the pulley is made of sufficient diameter to give room for a large bush, which is chambered externally, so that, when in position, it provides a large annular space for oil. The chamber is interrupted by three perforated ribs, which serve to carry the oil round when the pulley is in motion, and to stiffen the bush. From this chamber the oil, as it is carried up, passes to the bearing through a number of radial holes in the bush, being prevented from escaping at the ends by two circular grooves having oil-ways connecting them with the oil-chamber. The portion of the shaft upon which the pulley runs is thus regularly and automatically lubricated, and when supplied with a non-gumming, fairly neutral lubricant, only needs occasional attention.

Variable Load Bearings.—Crank pins, cross-head pins, and all bearings upon which the direction of the load is quickly reversed and the bearing surfaces thereby periodically parted, will carry extremely heavy loads. In such cases the lubricant is drawn in between the surfaces as they part, whilst the load remains on the bearing for so short a time that the oil-film is only partially pressed out. But these conditions do not at all times prevail, especially in locomotive engines, which have to start away with a heavy load behind them. The bearings upon which the iron or steel crank-pin is pressed have consequently, in such cases, to be made of very hard white metal, which will not squeeze out under the great pressure put upon it.

It must not be assumed, however, that the pressure on the crank-pin is measured by that of the steam on the piston, for, at ordinary running speeds, the inertia of the moving parts tends to equalize the pressures on the pin very considerably.

The load on a cross-head pin may be made much greater than that put on a crank pin, the angular motion of the cross-head and, therefore, the work done upon it, being much smaller.

A method of lubricating the big-ends of locomotive connecting rods is shown in fig. 114. Such big-ends seldom run for more than two or three hours without a stop, and a large oil reservoir is not required. The oil-hole is loosely plugged with a number of worsted strands secured to a twisted wire support. Upon this plug, the lower end of
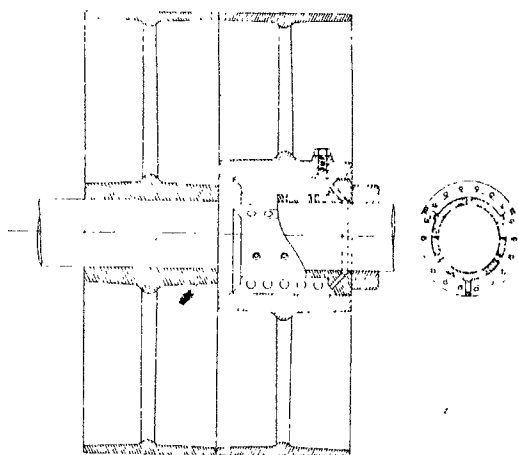
FIG. 113.

which rests upon a piece of sponge occupying a recess in the brass, so as to be in contact with the crank pin, the oil splashes as the crank moves. Another method of supplying oil to the big end, designed by H. Jessop, is shown in fig. 115. Here a loose central valve, having a very small lift, is placed in the oil-hole. This valve, except at very low speeds, is thrown from its seat at each revolution of the wheel, and allows a small quantity of oil to pass to the bearing. Such contrivances have been found to give very good results, as they do not easily become choked with sediment or gum up.

The lubrication of the connecting-rod big-ends of high-speed stationary engines, which have to work many hours without stopping, is generally effected from a fixed reservoir which supplies oil to the bearings as they rotate. A common appliance consists of a ring-shaped channel rotating concentrically with the shaft. Oil dropped

inside this ring is thre n by centrifugal force into a pipe arranged to deliver the oil to the bearing through a hole drilled in the crank pin. Another plan is to fix a knife edge above the connecting-rod lubricator, in such a position that it strikes an oily pad once during each revolution, and wipes off the oil with which the pad is moistened.

The eccentrics of steam engines work under much the same conditions as the crank ins. Owing, however, to their large diameter, the velocity of rubbing is greater, and they will not carry such heavy loads.

The reciprocating motion of an eccentric is generally so small, even when running, that ordinary siphon oil cups are easily filled by hand. When, however, the speeds are great, the oil is led through pipes leading from siphon lubricators to wipers. The eccentric straps of locomotives are usually made of steel or iron lined with white-metal which works upon cast-iron sheaves.
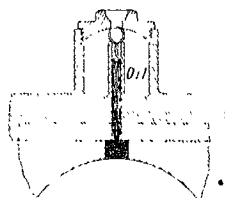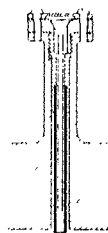
FIG. 114.   FIG. 115.

Pins with Reciprocating Motion.—In many cases pins have to carry a steady load, and the surfaces only move relatively to each other through a small angle. In some instances, the load that can with safety be put upon the bearing is only small; a greasy lubricant must, therefore, be used and the surfaces hardened. The slow reciprocating motion of the surfaces, and the constant pressure upon them, tends to expel the oil from the faces rather than to draw it between them. Such bearings are by far the most difficult to lubricate and keep in order, especially if every care has not been taken to make them of such metals as will work well together. If the oil be supplied by one groove running along the side opposite to that which carries the pressure, there is very little chance of its being able to spread itself over the rubbing surfaces. Two parallel grooves, one on each side of the centre line of the load, not very far apart, and arranged so that all parts of the surface shall be exposed to the oil resting in them during some portion of the motion, serve their purpose most satisfactorily.

Plane Surface Bearings.—The principal forms of bearings of this description are slide-blocks, collars, and pivots.

Slide Blocks.—When it is necessary to so constrain a moving piece,

or any part of it, that the motion shall be one of translation only, straight guiding surfaces termed slides and slide-blocks are generally used. Parallel link-motions, although they give a much smaller coefficient of friction when new, are more complicated, and the effects of wear are not so easily allowed for.

The loads at which oil pressure-films can form on plane surfaces being only moderate ones, slide-blocks are generally of cast iron working upon cast iron or steel. The slide-blocks are, however, sometimes lined with gun-metal or white-metal when the speeds are great. In America, chilled cast-iron surfaces have been introduced. The chilling is effected in diagonal strips separated by equally broad spaces of soft metal. This gives the surfaces that degree of unevenness which enables the oil to be trapped and so keep the surfaces apart. Oil-ways may be cut in long slide-blocks so as to distribute the oil over the surfaces and enable it to reach the edges ; but as the latter, if properly cut, do not quite reach the edges, the oil cannot readily escape.

The loads carried by slide-blocks range from 20 to 120 lbs. per square inch, according to the speed and the nature of the rubbing surfaces. At the lower pressures, cast iron works well upon cast iron, but when 100 lbs. per square inch is reached, gun-metal or white-metal upon hard steel must be used. When the load is light and the lubrication good, the wear is very small indeed, especially if the slide be a horizontal one and able to retain the lubricant.

Engine slides are usually made plane, but when the crank is not a fixture it is well to form the slides so that their surfaces are concentric with the centre line of the cylinder. The cross head then has freedom to rotate with every change of angle of the crank shaft. The lubrication of slides is best effected by siphon cups or other drop-feed contrivances, placed towards the ends of the bars, where the blocks pause, or only move slowly.

As a support for piston tail-rods, Messrs. Musgrave & Sons have introduced Buckley's device, which is a sheave rotating in an oil-bath. The rod rests upon the sheave, and the load is carried by the pin upon which it rotates.

Collar-bearings. — Collar-bearings, unlike slide-blocks, which only serve as guides for moving parts, and only have to bear intermittent loads, have, as a rule, to carry the thrust resulting from the weight of heavy shafts, or that produced by the pressure of the water on the blades of a screw. To enable them to carry the heavy weights this entails, the areas of their rubbing surfaces must be large, for, if the faces are not to actually rub against each other, and are to be separated by a viscous film, the loads per square inch must be small. With thrust bearings, and in cases where it is important that the efficiency should be high, bath lubrication is resorted to.

Tower's experiments on collar friction were made with very imperfect lubrication, only just sufficient oil being supplied to keep the surfaces from seizing. Under such conditions it appears that 70

or 80 lbs per square inch is the utmost that can be put upon such
a bearing with safety, and when the speed is great even smaller
loads than these must be used.

The collars which carry the loads in drilling machines, lathes, etc.,
have such heavy loads put upon them, that to prevent seizing, the
surfaces are made of the hardest steel, have numerous oil-ways cut
in them, and are lubricated with good fatty oils. Small bearings
with hardened faces, such as the spindles of drilling machines,
where the load is taken off occasionally, have steel faces which often
work under pressures as high as 300 lbs. per square inch, and, in
exceptional cases, as much as half a ton per square inch has been put
on a collar for a short time.

To ensure the proper lubrication of the faces of the thrust blocks
against which screw-shaft collars work, the thrust block faces are
cut away in such a manner that the collars are exposed in places
and dip into an oil-bath, or press against an oiled pad. In this way
fairly perfect lubrication is secured, provided the load be not greater
than 70 lbs. per square inch. However, as the efficiency of a thrust
block at the best is not high, the heat liberated is great, and the
block must, when the bearing is a large one, be kept cool by a
water jacket.

Pivot-bearings. — When the thrust to be carried acts upon a
vertical shaft, instead of carrying the load on collars the end of the
shaft may rest upon a circular face or pivot-bearing. This form of
bearing permits of bath lubrication, for the footstep may be so
designed that it forms a vessel which can be kept full of oil.

Fig. 116 shows a bearing surface such as Tower used. The oil is
admitted through the centre hole and passes into two radial grooves.
From these grooves the lubricant is carried between the surfaces,
and is expelled by the pressure upon the pivot. The track of the
oil varies at different parts of the surface, a portion being expelled at
the edges. This sets up a continuous circulation of the oil from the
centre of the bearing to the margin of the footstep, and up between
the cylindrical portion of the bearing and surrounding bush.

The only reliable experiments on the friction and sustaining power
of pivot bearings are those made by Tower with this pivot. In
these experiments are given the greatest loads which he found a
pivot-bearing would carry without actual abrasion of the surfaces
taking place. For the actual results, see p. 70.

Fig. 117 represents a footstep-bearing somewhat similar to one
designed by Ford Smith. Here the circulation is as shown by
Tower, but the actual bearing consists of four discs of hardened steel
all perfectly free to revolve with the pivot. Through the centre of
all four washers is drilled an oil hole, and radial grooves are cut in
the faces. The passages C enable the oil to circulate between the
washers and up the side of the shaft. By using four washers, five
friction surfaces are formed, and the films are increased in number
to the same extent.

This enables the temperature of the films to be kept more nearly
that of the masses of metal, and should one become a little over-
heated and tend to seize, the other faces move relatively faster
and allow it to cool again.   As a means of relieving any local
pressure which might result from the springing of the shaft, it has
been suggested that one of the loose washers should be made convex
on one face, as shown, so as to fit in a concave face on the opposing
washer or pivot.

When the pressures exceed 160 lbs. per square inch, the surfaces
must be made of hardened steel working upon a similar face, or upon
dense cast iron or bronze.   Should the load per square inch exceed
300 or 400 lbs., a force pump must be resorted to, and a continuous
stream of the lubricant forced between the pivot and footstep.   As
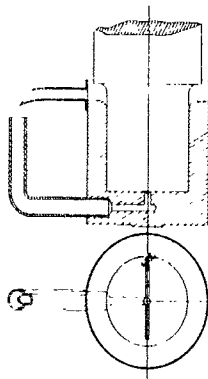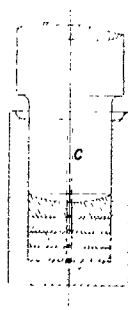
FIG. 116.   FIG. 117.

much as 1 ton per square inch can be supported by this means
without any difficulty.

Piston rod Packings.—The conditions under which the bearing
surfaces of piston rods work, although the surfaces are of cylindrical
form, are very different from those of journals or shafts, for the motion
is a longitudinal instead of a rotary one.   It is seldom that they are
used as guides, the load on them being restricted to that resulting
from the devices used to take up the wear and keep the joints steam-
tight.   It is the slide-blocks and piston head which should be made
to act as guides, and if these be not accurately fixed in line, or
become a little loose by wear, the packing will blow, unless it is made
free to move laterally with the rod.

In fig. 118 is shown a form of metallic packing, known as the
'United Kingdom Metallic Packing,' which has given good results on
locomotives.   Split rings of white-metal, of triangular section, are
held in a brass frame, which is free to slide laterally against a surface
upon which it is pressed by the steam and a strong spring.   As the

white-metal wears away it is kept in contact with the rod by the pressure of the spring. For such packings to work satisfactorily the rod must be quite true, and free from shoulders at the ends. Good lubrication is also absolutely necessary. It is generally supplied by means of a small siphon or drop lubricator to a pad resting upon, or even surrounding, the piston rod, which is thus kept moistened with oil.

Rolling Contact Bearings.—*Ball Bearings.* — Although under the conditions of running which usually obtain in practice well lubricated plain bearings give good results and low coefficients of friction, yet under certain conditions better results can be obtained with ball or roller bearings. The former have a very extended use for all types of cycles, various kinds of clock-

FIG. 118.

work, etc., whilst recently they have found a constantly extending field for use on motor cars of various descriptions.
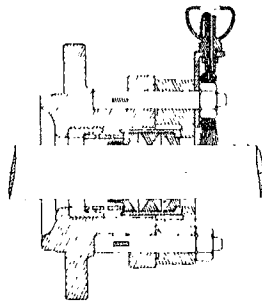
The coefficient of friction is not affected by changes either in the load or speed, and only to a very slight extent by the viscosity of the lubricant, which only tends to replace solid friction by viscous friction, and thus reduce wear.

In all cases where ball bearings are used, it is absolutely imperative that there should be freedom from shock, for a smart blow will either break the balls or destroy the accuracy of the surfaces upon which they run. Failure to grasp this essential fact led to considerable trouble when, in the early days of automobile design, attempts were made to use ball bearings for supporting the axles of cars fitted with non-resilient tyres. Since the general introduction of pneumatic tyres, which has coincided with a marked improvement in the manufacture of ball bearings themselves, little trouble has resulted from broken balls on vehicles. Although the crushing weight of a ball a quarter inch in diameter is as high as 5000 lbs., the load it will carry in general use without breaking is only about 200 lbs. ; the crushing load is proportional to the square of the diameter of the ball.

The ball bearings of cycles are arranged to be as dirt-proof as possible, and frequently are provided with an oil bath, these precautions allowing the bearings to be kept clean and well supplied with the lubricant. The balls run on contact surfaces, so designed that any wear can be taken up by lateral adjustment and an accurate fit secured. The ball paths in bicycles are usually made concave, their radii being somewhat larger than that of the balls, the latter having two points of contact. When the distance between the races is carefully adjusted, and the balls are accurately centred between the faces, the frictional resistance is that due to rolling only, and the

pressure on the balls is merely that due to the load. If, however, a bearing is badly designed or made, and the balls work slightly out of position, they jam, and the load upon them, and consequently the friction, increases. Fig. 119 shows a bicycle bearing with three points of contact, but as a rule two only are employed, although the type shown prevents any possibility of the balls becoming displaced.
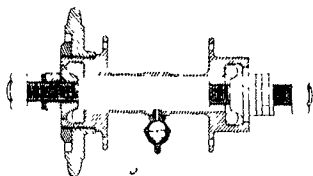
With motor car work no means of adjustment is usually allowed, for it is realised that when either a ball, or its race, wears, additional friction is likely to be set up, and the best course is to change the bearing. The accuracy of workmanship and hardness of the wearing surfaces is so great that little trouble is experienced in this way. It has been found most advantageous for this class of work to employ separate bearings for taking up the horizontal and vertical loads respectively. The type used for taking the load of the car is usually similar to fig. 120, which represents the D.W.M. ball bearing made by Messrs. Ludwig, Loewe & Co., the radius of the race being, as with cycle work, somewhat greater than that of the ball. In some cases the balls are allowed to touch one another, although this is impossible in the type shown, as the balls could not then be inserted ; the more usual custom, and the better practice, is to keep the balls separate, either by placing them in a cage, or separating them by springs and pads. This was first suggested by Conrad.[1] The number of balls is limited to as many as will fill one half of the bearing, which is then assembled and the balls distributed by inserting the elastic distance pieces. In this way, all openings and joints which would be needed for the insertion of a larger number of balls are done away with and the perfect continuity of the races is not interfered with. In order to take the horizontal thrust, in some cases a V-shaped race is employed, whilst in others the usual radius shape is used. In motor car construction it often happens that a bearing has to resist both load and side thrust, and in this case a single set of balls is not satisfactory and a compound bearing has to be employed. A type of this class is shown in fig. 121, which represents the practice adopted by the Hoffmann Manufacturing Co., who have made a speciality of this work for some time.

Roller Bearings. In cases where the load is steady, but too great to allow of the use of balls, rollers are now frequently and increasingly used. The great advantage which they possess over plain bearings for some purposes arises from the small frictional resistance to motion which they offer at very low speeds. This is a very important consideration where heavy structures, such as swing bridges, have

to be moved, or where any heavy machine or vehicle has to be
started and stopped frequently. 'Great Paul,' the big bell at St.
Paul's Cathedral, which with its headstock weighs nearly 25 tons,
has now been supported satisfactorily on roller bearings for over ten
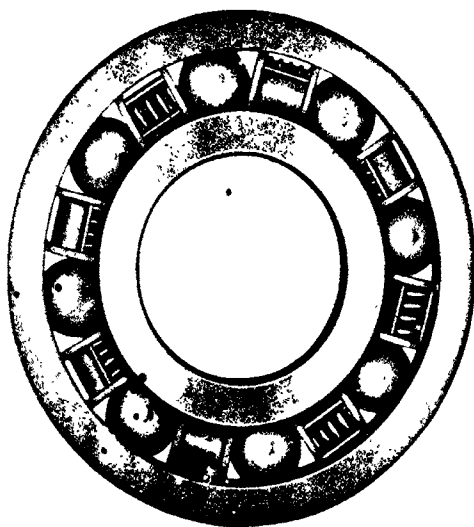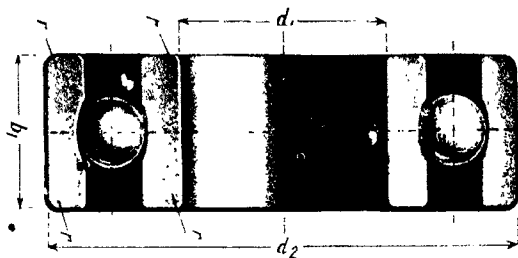
Fig. 120.

years, and it is stated that the bearing is as good, and the bell as
easily worked, as when first put up.

In addition to the application of this class of bearing to shafting
and similar parts of machinery, it has during the past few years
been employed on vehicles of various kinds. In order that a roller
bearing may work successfully, it is essential not only that the rollers

should be parallel in themselves, but that there should be no chance of their axes becoming anything but parallel with the axis of the shaft.

Fig. 122 shows a bearing made by the Empire Roller-Bearings Co., Ltd., in which the above-mentioned condition is provided for by fixing the rollers in a floating gun-metal cage which itself slowly revolves round the shaft. The particular bearing shown in fig. 122 is for a railway vehicle, and fig 123 shows a section of a similar one used on the passenger stock of an English railway. In the latter illustration it will be seen that the end thrust is taken up by a bearing plate, and it is

Fig. 121.   Hoffmann Ball Bearing.

essential that the rollers and the shaft itself shall be true in order that this thrust may not become excessive. Roller bearings of a somewhat similar type are being successfully employed on tramcars, heavy motor cars, etc., and one great advantage which they have is the fact that they require very little lubrication, only sufficient

Fig. 122.—Empire Roller Bearing.

lubricant being needed to prevent the bearings from rusting. The first cost, and the difficulty, in the past, of preventing excessive end thrust, have been the only obstacles preventing this type of bearing from being very extensively adopted.

In the Hyatt roller bearings a *flexible* roller is used, which is made of a strip of steel wound into a coil or spring of uniform diameter. The chief advantages claimed for this construction are that the flexibility of the roller enables it to adapt itself to any slight

irregularities in the journal or box, whilst the hollow roller serves as
an oil reservoir.

The results of a number of friction tests with this roller bearing
were given by Prof. A. L. Williston, in a paper read before the
American Society of Mechanical Engineers in 1905.[1] In one series
of tests, carried out for the purposes of a proposed incline travelling
roadway, the coefficient of friction of the Hyatt roller bearings, cast-
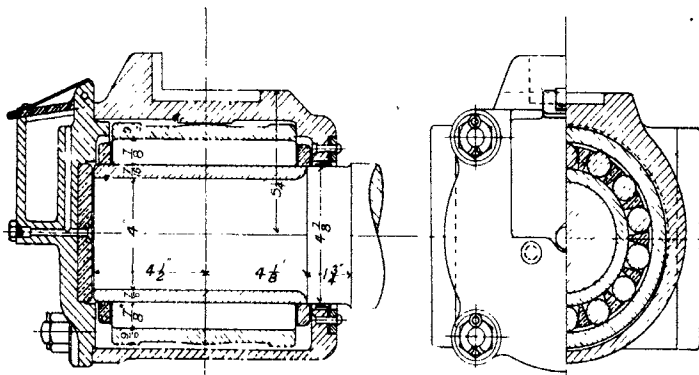
FIG. 123.—Empire Roller Bearing.

iron bearings, and bronze bearings were compared. In order to
imitate, as far as possible, the conditions of practice, the shaft used
in all the tests was 1·496 inches in diameter, the speeds varied from
128 to 585 revolutions per minute, the total load ranged from 1900
to 8300 pounds, and the same grade of machinery oil was continu-
ously fed to the bearings under a head of about one inch. The
following results were obtained :—

Bearings.	Average Coefficient of Friction.	Revs. per min.	Average Coefficient of Friction.	Revs. per min.	Average Coefficient of Friction.	Revs. per min.
Hyatt rollers, .	0·0114	130	0·0099	302	0·0147	585
Cast iron (plain),	0·0548	128	0·0592	302	0·0683	410
Bronze (plain), .	0·0576	130	0·0661	320	0·140	582

At the lowest speed, the cast-iron bearings seized at 8300 pounds
pressure, and the bronze bearings at 3500 pounds. At the middle

[1] *Trans. Amer. Soc. Mech. Engineers*, vol. xxvii p. 499.

speed, the bronze bearings seized at 5900 pounds. At the highest speed used, the cast-iron bearings seized at 5900 pounds and the bronze bearings at 3500 pounds. The roller bearings did not seize at all in any of the tests.

In a further series of tests at speeds of 185 and 215 revolutions per minute, the friction was measured under very much heavier loads (up to 23,500 lbs.) than could be carried by either cast iron or bronze plain bearings, and proved that these flexible roller bearings are specially advantageous when heavy loads are encountered.

APPLIANCES FOR LUBRICATION.

Needle, Siphon, and Drop-feed Lubricators.—Although the old forms of lubricators are being dispensed with to a large extent in favour of more perfect automatic contrivances, securing more or less perfectly the advantages of bath lubrication, it is unlikely that they will be displaced entirely, for there are cases in which the conditions of working are such that the lubricant cannot be recovered, and must be supplied continuously in small quantities. Slide bars and piston

rods are cases in point. Needle, siphon, and drop-feed lubricators are largely used for these and other purposes, and for shafting.

The *needle lubricator* shown in fig. 124 consists of an inverted glass reservoir with perforated wooden stopper, in which a metallic needle fits rather loosely. This needle rests upon the shaft. The up-and-down movement of the needle, caused by the rotation of the shaft, slowly causes the oil to be expelled from the reservoir, and allows its place to be taken by air which works up past the needle. Changes of temperature are apt to cause considerable irregularity in the working of this lubricator.

The *siphon lubricator*, as used for lubricating a piston rod, is shown in fig. 118. It consists of a shallow reservoir in which the oil is stored, and

Fig. 124.—Needle Lubricator.

a central tube, leading to the part to be oiled, and having its upper orifice raised a little above the oil surface. Through this tube is passed a wick of cotton or worsted, one end of which is immersed in the oil and the other end hangs downwards. Up the capillary spaces between the fibres of the cotton or worsted the oil makes its way,

and passing down the tube, converts the capillaries into a number of small siphons, which slowly drain the oil out of the reservoir, and thus lubricate the opposing surfaces below. The theory of this action is fully described in the chapter on 'Superficial Tension,' p. 30.

The *sight drop-feed lubricator* (fig. 125), made by Messrs. Mather & Platt,[1] consists of a small reservoir having a passage leading from the bottom, which can be closed by a tap in which is a small valve which can be regulated as desired. The discharge orifice terminates in a nozzle protected by a short glass tube, which enables the engineman to see the exact rate of feed. Such lubricators are liable to be stopped by hairs, mucilage, dirt, etc., especially if the valve and outlet orifice be at the bottom of the oil-cup, and the oil be not strained.

A *combined sight drop-feed and siphon lubricator* is shown in fig. 126. The lower vessel, M, which has a small capacity, is provided with the necessary number of siphon tubes (the one illustrated has three) for containing the cotton or worsted trimmings or wicks T. This vessel has a hinged lid L, which affords a ready means of access for fitting and examining the trimmings; the lid is kept closed by a spring.
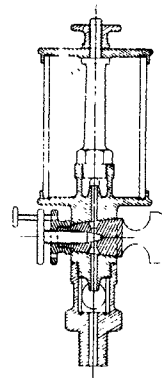
FIG. 125.—Drop Lubricator.

The tube U conducts the oil direct to the point of application, or, as in the case of an axle-box, to another oil-well of small capacity, from which oil is taken by further trimmings to the part to be lubricated. The drop lubricator, which delivers its oil into M through the sight glass G, consists of an oil vessel A fitted with a valve V, which is used to regulate the supply of oil from A to M. In the illustration, this valve is shown closed.

To open the valve V, the end of the spindle is raised, and, after turning it through 90°, the knife edge at K is allowed to drop into the groove which is cut in the top of the adjusting screw B to receive it. The flow of oil from A to M is regulated by raising or lowering the nut B until the desired adjustment has been attained ; B can then be secured by tightening the nut C. The spring S is for the purpose of closing the valve when the knife edge is released from the groove in the top of the nut B. The seat of the valve V is higher than the bottom of the lubricator, thus forming a cavity which prevents sediment from being washed on to the valve seat ; the bell H is provided to prevent suspended matters from settling on the valve seat. A number of air holes, O, are made in the top of the bell.

[1] A. Howat, Eng. Patent No. 20205 (1893).

The valve is provided with a loose pin P, having a ball and socket connection ; the body of the pin fits the small passage between the face of the valve V and the sight tube, the motion of the machinery

or locomotive to which the lubricator is fixed causing the pin to vibrate and keep the passage free and the supply of oil uniform. When filling A with oil, the wing nut D is unscrewed until a hole through it coincides with the hole E.

With the ordinary siphon lubricator the supply of oil to the bearings continually diminishes as the level of the oil in the reservoir falls, but with this combined lubricator it is kept practically constant, and by varying the number of strands in the trimmings the lubricant can be distributed to the various bearing surfaces in any proportion desired.

Automatic and Mechanical Drop-feed Lubricators. —Lubricators of this type differ from the foregoing, inasmuch as they are brought into action by the movement of the machinery to which they are attached, and they automatically cease to feed oil as soon as the machinery stops.

Threlfall's automatic lubricator for locomotives, made by Messrs. W. H. Bailey & Co., of Manchester (fig. 127) has an inner

Fig. 126. – Combined Sight Drop-feed and Siphon Lubricator.

chamber containing a brass ball with concave seating. Leading from the oil reservoir to this inner chamber is a passage, terminating in the centre of the ball-valve seating. Another passage leads from the inner chamber, through the shank of the lubricator, to the bearing. The tube leading from the top of the valve chamber to the under-side of the lid is for the admission of air, and serves also for flushing the

bearing with oil, if required.   The cone valve regulates the supply of
oil passing from the reservoir to the valve chamber.

When the locomotive is in motion, the ball rolls loosely on its
seating, thus admitting oil to the bearings.   When the engine comes
to rest, the ball remains upon the centre of the concave seat, thus
closing the oil-supply pipe.

Fig. 128 shows a cylinder lubricator on the same principle.   It
has a second ball valve in the shank, the object of which is to
prevent steam from entering the lubricator.   This valve has an
upper and a lower seating, the latter having fine slots cut in it in order
to allow the oil to flow past the valve during the exhaust stroke, or
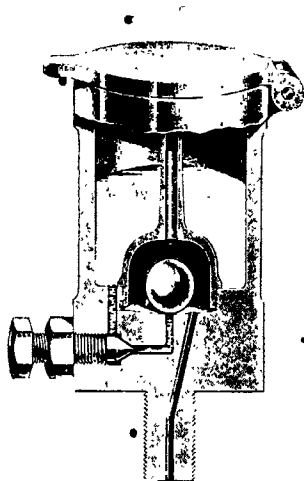
FIG. 127.—Threlfall's Automatic   FIG. 128.—Threlfall's Automatic
        Lubricator.   Lubricator (Steam Cylinder Pattern).
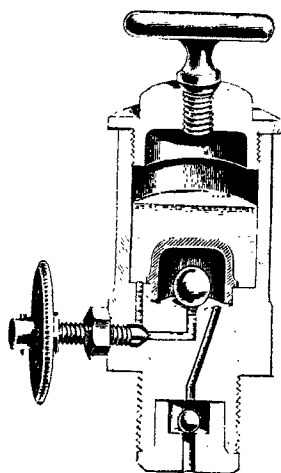
when steam is shut off.   When steam is admitted to the cylinder,
the valve is forced against the upper seating and closes the passage
communicating with the upper ball-valve chamber, thus preventing
the steam from entering the lubricator.

Stephens' 'Octopus' sight-feed lubricator, made by Messrs. B. R.
Vickers & Sons of Leeds, is illustrated in section in fig. 129.   A is
the oil chamber, into the bottom of which is ground a gun-metal
spindle B.   In the spindle are openings into which are introduced
the screw plugs F by adjusting which the oil supply to each of a
number of bearings can be regulated.   The exact amount of oil
which can fill each cavity above the plug is discharged into the
corresponding bearing at each revolution of the spindle, through one
of the sight tubes H H, the air tubes E E allowing air to enter the

cavities in the spindle and take the place of the oil which runs out.
Oil can be poured down these air pipes into the bearings, if necessary.

The spindle is rotated by means of a ratchet C and lever connected
with a moving part of the engine or machine, and the number of
revolutions of the spindle can be varied by means of a movable eye
on the ratchet lever. The ratchet or lever can be replaced by
friction clutch or worm gear, if desired. A gauze screen, G, prevents
foreign matter in the oil from entering the bearings. Lubricators of
this type effect a great saving of oil.
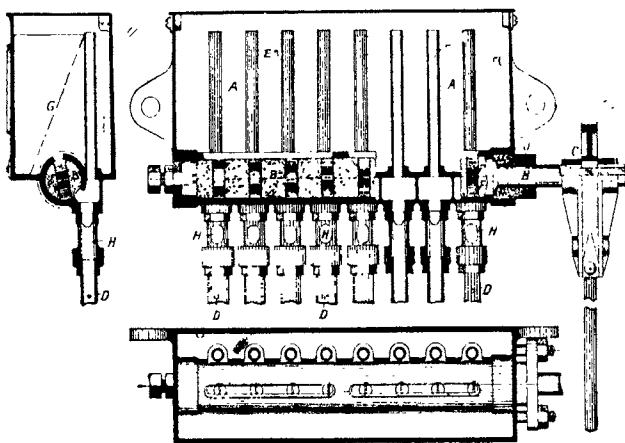
Fig. 129.—Stephens' 'Octopus' Sight-feed Lubricator.

Mechanical 'Pressure' Lubricators.—Lubricators of this type
supply oil to any part of an engine under pressure, and to the
bearings.

The *'Serpollet' sight-feed mechanical lubricator*, made by Messrs.
Schäffer & Budenberg of Manchester, shown in section in fig. 130,
has a piston actuated by a ratchet and lever to which a to-and-fro
motion is communicated by means of a double cam. The piston is
provided with two slots, a longitudinal slot by which the oil is
delivered successively to the different outlets (only one shown in the
figure), and an oblique slot by which the oil is drawn into the hollow
piston from the oil reservoir during the suction period. In addition
to the working piston there is a second shorter one held down by a
spring, which serves to relieve any excess pressure. The tension of
this spring can be varied, by turning the spindle projecting through
the stuffing-box to suit different feed pressures. The oil from each
outlet rises through a sight glass, of which from two to eight are
connected to one lubricator and supply oil to as many bearings.

Another lubricator of this type, also made by Messrs. Schäffer & Budenberg, is *Franke's mechanical lubricator*, shown in fig. 131. The ratchet wheel S is rotated in the usual way by connecting the
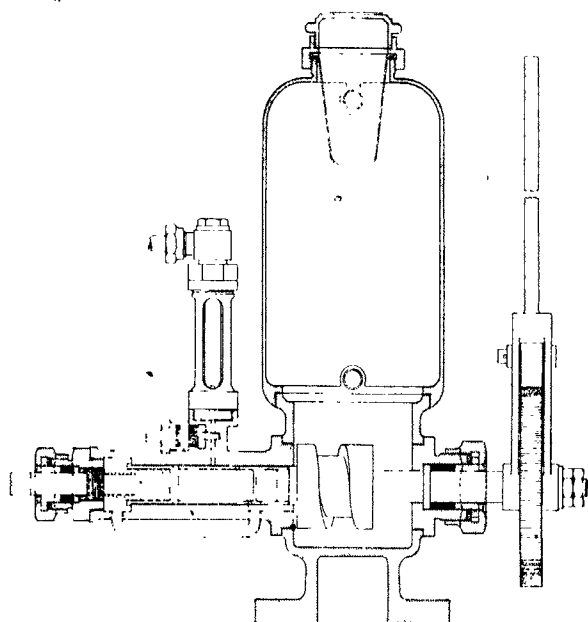
Vertical Section.
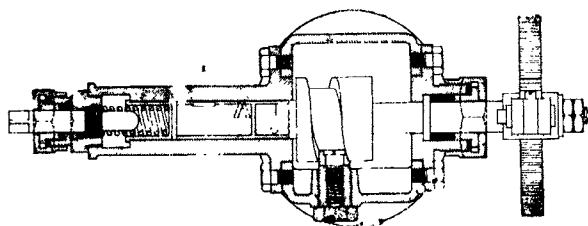
Horizontal Section.

Fig. 130   'Serpollet' Sight-feed Mechanical Lubricator.

lever H with any suitable part of the engine. The cylinder C, containing a plunger K, is rotated by the ratchet wheel spindle. During each revolution of the cylinder the two ends of the plunger

alternately come in contact with the projecting end of the pin a, and thus the plunger is moved to and fro, producing a pumping action by which the oil is alternately drawn into the cylinder and forced

Horizontal Section.   Vertical Section.
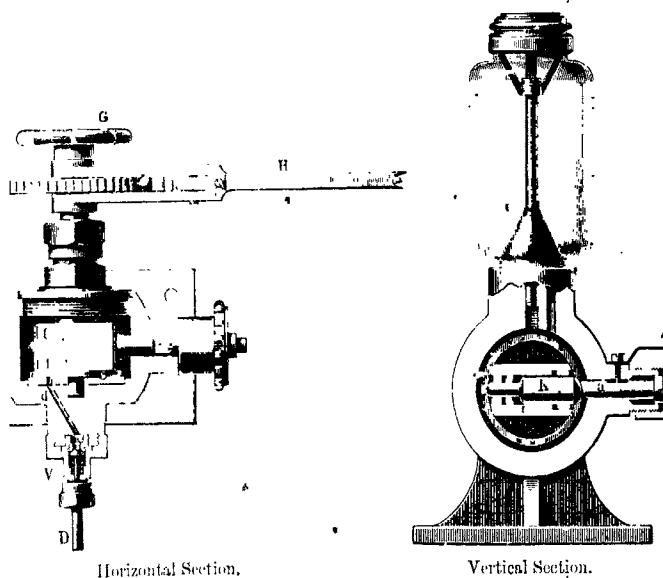
Fig. 131.—Franke's Mechanical Lubricator.

forward to the delivery.   For this purpose the cylinder C is provided with a passage b which alternately communicates with the oil reservoir through the suction passage s, and with the delivery pipe D through the passage d.   By turning the nut O the pin a can be adjusted to vary the stroke of the plunger K, so as to give the required feed of oil.

Fig. 132.

Grease Cups.—When it is considered desirable to use grease as a lubricant, the Stauffer 'tell-tale' lubricator can be recommended.   This is shown in fig. 132.   The rate of feed is regulated by the screw G, the small piston D, being forced down by the spring, indicates when it is necessary to screw down the cylinder A.

Pad Lubrication.—For the lubrication of journals, woollen or felt pads, kept moistened with oil and pressed against the journal, are now largely used. Journals or shafts should be kept uniformly moist with oil, but

should not receive such a quantity as to be thrown out in any great volume at the ends of an ordinary pedestal or axle box, and wasted. But when proper means are adopted for preventing lateral waste, the pads may be partially immersed in the lubricant or may obtain their supply of oil through wicks which dip into it.

Even when the old methods of siphon lubrication are adopted, pads are frequently used as auxiliary lubricating contrivances, since they remain moist for long intervals of time and keep the bearings from becoming overheated in the event of the siphon wicks, or oil cups, ceasing to supply the lubricant.

So unquestionable have been the advantages gained by the oily pad system of lubrication, that it is now almost universally used for quick-running railway vehicles. Not only is the friction kept uniformly low and the consumption of oil remarkably small, but the number of heated journals has become almost a vanishing quantity. Quite a number of the bearings illustrated in this chapter have the lubricants supplied by pads.

Fig. 110 (p. 416) shows the journal and axle-box of a railway vehicle lubricated in this manner. The woollen pad is attached to a light steel framework held up against the journal by means of light springs, and is supplied with oil by means of cotton feeders dipping into a bath of oil at the bottom of the box. In the 'Armstrong' oiler the pad is made of a mixture of wool and cotton, and is prevented, by means of *lignum ritæ* studs, from becoming flattened and glazed through excessive pressure on the journal.

In place of the pad and steel framework, the lower part of the axle-box may be filled with a mixture of horsehair, worsted, and cotton. The elasticity of the hair keeps the mixture open and pressed against the journal, the cotton and wool soak up the oil from the bottom of the box and supply it to the friction surfaces.

Experiment has shown that the more fully saturated the pads, etc., are kept, the smaller is the friction, and that the best result is obtained when the journal actually revolves in a bath of oil. From the descriptions of bearings on pages 410 to 430 it will be seen that it is possible to take advantage of the low frictional resistances which perfect lubrication gives without either incurring waste of oil or undue complication of parts. At the present time, the scientific design of bearings can perhaps only be regarded as in its infancy. But it is inevitable that, as the true principles of lubrication come to be better understood, the use of solid or semi-solid lubricants will be largely given up, and for all quick moving machinery the oil-bath or its equivalent will be almost universally used.

Pump Circulation.— Instead of placing a reservoir beneath or above each bearing, and allowing the latter to automatically lubricate itself, the plan is often adopted of supplying the bearings of engines, dynamos, etc, in an engine-house, from one or more raised tanks into which the oil is pumped from a common well, to which the lubricant gravitates as it runs off the brasses. By this means the oil is used over and

over again, and can be strained, clarified, and replaced as desired.
This method involves the use of a rather intricate set of supply and
return pipes, and the bearings must be designed so that the waste oil
may be collected without loss as it runs off the steps, slides, etc.

In *Parsons' system* the oil is supplied to the bearings under a
slight pressure, varying in different instances from a few inches to
several feet, but which is in all cases just enough to allow the oil to
flow freely through the bearings, from which it carries off the heat
generated by friction; it is then cooled by a tubular cooler before
being returned to them. As the oil is nowhere exposed to the outer
air, but circulates only in a closed system, it collects no dirt and
does not require filtration, but circulates over and over again con-
tinuously, the entire supply passing through the journals every few
minutes. As instances of the astonishing economy of oil thus
realised, A. M. Mattice, in a paper read before the American Society of
Mechanical Engineers,[1] cited two 100-kilowatt steam turbines of the
Parsons' type running at 3600 revolutions per minute, one of which
used only 50 gallons of oil in six months, and the other one 55
gallons; whilst at another plant, consisting of two units rated at
750 and 400 kilowatts respectively, only three barrels of oil were
used in sixteen months. The turbine steamer *Virginian*, according
to Mattice, made four successive round trips between Liverpool
and Montreal without any addition of oil to her tanks, and the
supply was still not appreciably diminished from its initial figure of
115 imperial gallons. In this case the whole supply passed through
the bearings every four minutes. The figures quoted are, of course,
those for the turbine bearings only, since the line shafting had
ordinary lubrication.

In the '*Bellis' system of forced lubrication* the oil is pumped into
the bearings under considerable pressure. The illustration, fig. 133,
shows a Bellis & Morcom engine lubricated in this manner.   A
pump A, placed in the crank pit, supplies oil under pressure to the
main bearings, crank-pin bearing, cross-head gudgeon pin, guide shoe
faces, and eccentric sheave. Two sections of the oscillating pump
are shown. The plunger, closely fitting the pump barrel, is actuated
by being attached to the engine eccentric strap. The pump barrel
is mounted on trunnions, and the oscillating motion imparted to it
by the eccentric brings the port in the circular face at the bottom
of the barrel alternately opposite to the suction and discharge ports
in the fixed portion of the pump. The pump is kept continually
immersed in oil, and takes its supply of oil from the crank pit through
a cylindrical strainer, round which is wrapped fine gauze wire to
prevent grit and dirt from getting into the bearings. The delivery
branch of the pump is connected to a main supply pipe B, from
which branch pipes are led to nipples screwed through the cap into
the brass of the main bearings. The method of conveying the oil

[1] *Trans. Amer. Soc. Mech. Eng.*, vol. xxvii. p. 469; also *Engineering,* May 11th,
1906, p. 621.

from the main bearings, and the direction of flow, are clearly shown in the illustration.

A circumferential groove C is turned in the brass, from which a radial passage D, drilled in the shaft, conducts the oil to a similar circumferential groove E, in the crank-pin bearing; from the groove
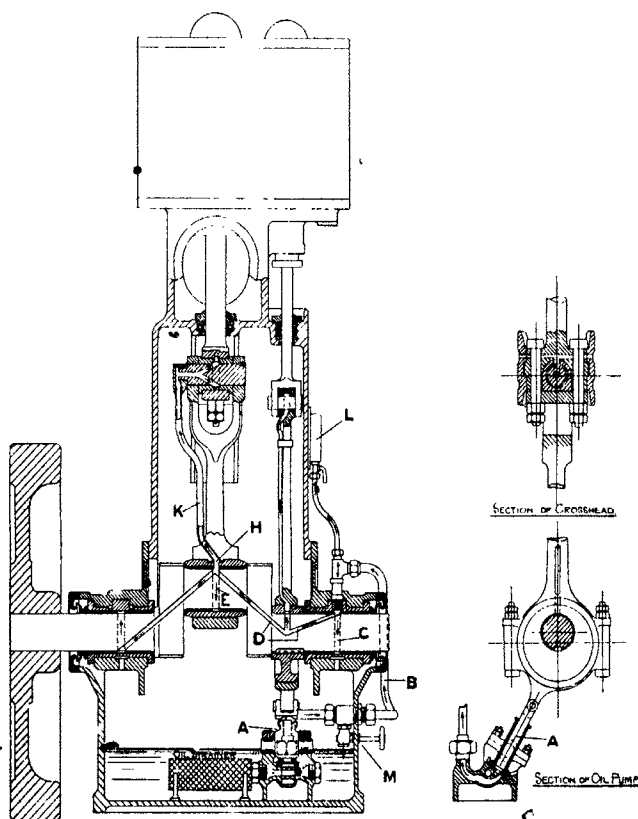
FIG. 133.—Bellis' System of Forced Lubrication.

in the crank-pin bearing the oil is conducted by a passage H and pipe K to the interior of the cross-head pin, and thence by a similar arrangement of circumferential groove to the guide shoe.

The lubrication of the eccentric rod and valve rod pin is dealt with on similar lines. From the main oil-pipe, a pipe is led to a pressure gauge L, reading up to 50 lbs. per square inch, which shows at a

glance whether the oil pressure is being maintained—the usual
pressure being from 10 to 20 lbs. per square inch. If the pressure
in the lubricating system of pipes be too great, an oil-relief valve M,
fixed on the main supply pipe, is slightly opened, and permits a
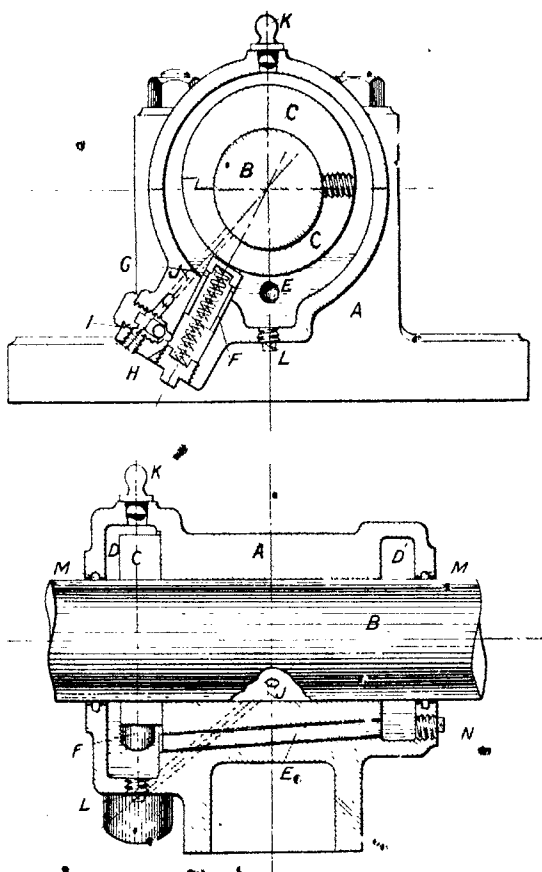
Fig. 13f.—Tilston's Automatic Forced Lubricator.

small quantity of oil, which has passed through the pump, to be
returned to the reservoir.

Tilston's automatic forced lubricator, shown in fig. 134, is an
ingenious application of the same principle to line shafting and other

bearings. A is the cast-iron bearing, B the shaft, C an eccentric keyed or screwed to the shaft, by the revolution of which the pump plunger F is reciprocated. When the plunger is at the top of its stroke, the oil in the chamber D passes through the holes G into the space beneath the plunger, and is forced thence by the return stroke past the non-return valve I and through the outlet J into the space between the shaft and bearing, whence it escapes into D or D′, to be pumped over and over again. The leather washers M M prevent the oil from travelling along the shaft and getting lost.

Splash Lubrication. To secure the advantages of good lubrication as well as to keep out grit and dirt, many kinds of mechanism are completely enclosed in cases containing the lubricant, which is thrown about by the moving parts, drenching all the exposed rubbing surfaces, and freely entering the oil-ways provided. In this way not only is the oil used over and over again, but perfect lubrication is secured, and, as previously pointed out, particles of grit and dirt are prevented from mixing with the oil and grinding away the rubbing surfaces.

The central-valve vertical engines of Messrs. Willans & Robinson (fig. 135) have the whole of the moving parts enclosed in this way, and perfect lubrication is secured for all parts. The bed plate forms a reservoir in which is placed oil and water. At each revolution of the crank the lubricant is thrown about the upper portion of the chamber, lubricating the connecting rod ends, valve-gear, main bearings, etc. These engines may, therefore, be allowed to run with full load, and without a single stop, for more than a month at a time, for the wear is exceedingly small, and all the parts can be kept well supplied with oil.

Vertical gas and oil engines, including high-speed motor car engines are frequently lubricated in a similar manner, oil alone being used in the chambers.

Steam Cylinder and Valve Lubrication.--*Grease Cup.*--Grease cups are now seldom, if ever, used for lubricating steam cylinders for they are not capable of feeding suitable oils with the necessary regularity, and it is now recognized that tallow, and greases containing vegetable or animal oils or fats, should not be used in cylinders. A cup designed like a grease cup may, however, be used as a ready means of introducing a charge of lubricating oil into a steam space against the steam pressure, and there are instances when it is advisable for this to be done. The usual design of such a lubricator is shown in fig. 136. By opening the upper tap whilst the lower one is closed, the central globe may be filled with oil. On shutting the upper tap, and more or less opening the lower one, the lubricant is allowed to flow into the steam space below, whilst the steam flows into the globe.

Roscoe Water-displacement Lubricator.--It has been found more convenient and more economical to replace the above-described simple method by an automatic contrivance which will feed the

ubricant slowly, as it is required. One of the earliest and most
satisfactory instruments of this class for locomotive engines is the
Roscoe[1] lubricator shown in fig. 137. The delivery pipe, which
passes some distance into the steam pipe, must be of such diameter
that both the oil from the lubricator and the water resulting from
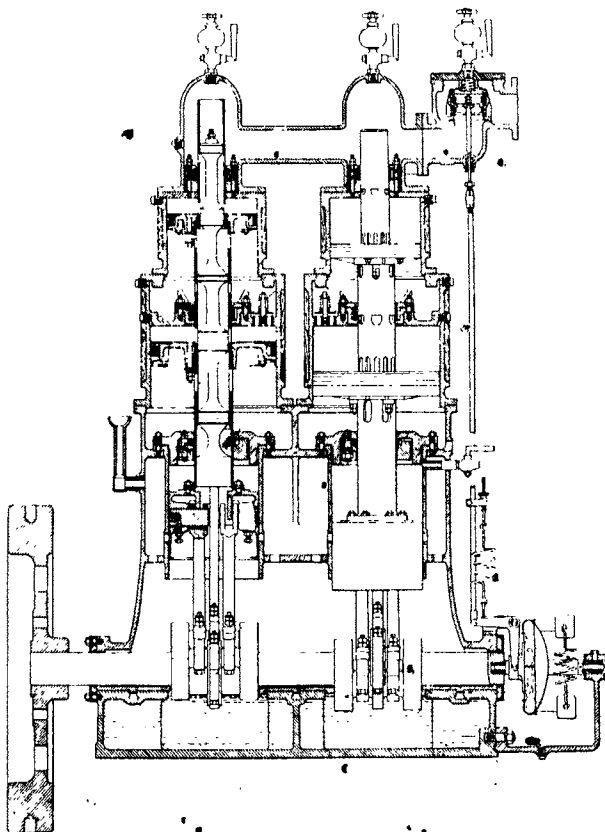
Fig. 135.

condensation can flow away freely along the bottom, and allow live
steam to enter along the upper part of the bore.

In many of these forms of lubricator designed for cylinder work
the oil is displaced from the lubricator by the weight of a column of
water produced by the condensation of steam from the boiler or steam

[1] James Roscoe, Leicester, Eng. Patent No. 1337 (1862).

pipe. Should there, in this form of lubricator, be a deficiency of water resulting from a check in the rate of condensation, the lubricator may cease to feed. When the boiler is supplied by means of an injector, air, as well as water, is thrown into the boiler. Air thus introduced, remains in the pipes leading to the lubricator, or even in the upper parts of the lubricator condenser, and by remaining there and preventing steam from entering, checks condensation and stops the feed of oil.

A pipe too small in diameter, or not having a regular slope towards the steam pipe, will become choked with the liquid and prevent the lubricator working.

The Roscoe lubricator consists of a chamber which can be filled
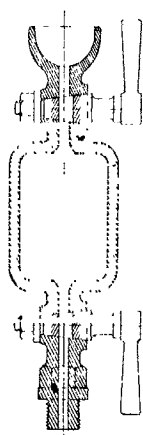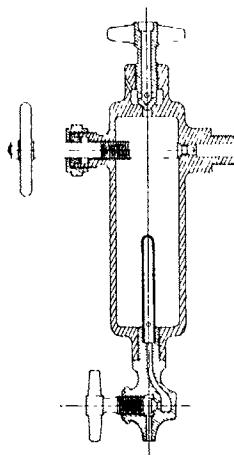
FIG. 136.   FIG. 137.

with oil from above. Near the top of this chamber is the delivery passage which can be opened or closed to any desired extent by means of a valve. There is also in the centre a vertical tube, the upper end of which is closed, and the lower end perforated to admit water or oil. Upon the vessel being filled with oil, the tube remains full of air until the delivery valve is opened, when, the steam entering the lubricator, the air is compressed. The steam then rapidly condenses, and the water falls to the bottom. So long as the engine is running, the delivery valve is left slightly open, with the result that steam or water slowly enters the lubricator, and the oil slowly finds its way out. Should steam be shut off, the pressure in the lubricator is relieved, the air expands in the central tube, and a quantity of oil is driven out which serves to keep the parts lubricated until steam is again turned on. The amount of opening which

must be given by the driver to the delivery valve when the lubricator is fixed on a locomotive depends upon the number of stops which have to be made by the train, the temperature of the air, and the extent to which the steam is throttled by the engine regulator. An experienced driver can judge these points very satisfactorily, and obtain good results without waste of oil.

Automatic Engine Cylinder Lubricator. — A water-displacement lubricator of somewhat different type, made by Messrs. Schäffer & Budenberg, is shown in fig. 138. Here the steam enters by the central tube and the condensed water displaces the oil, which is thus forced out through the same tube. The valve shown on the right serves for regulating the steam admission and oil discharge, whilst the opposite valve discharges the condensed water either outside, through a tap, not shown in the figure, or into the cylinder. This lubricator can, therefore, be used as a grease cup if required. It has a glass window on either side.
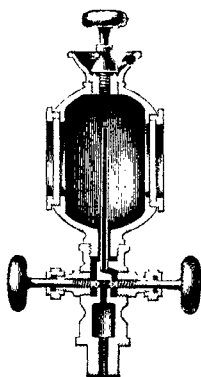
For steam cylinders, during the last few years, sight-feed lubricators have been very largely used. Of these lubricators, and there are numerous designs upon the market, only a few can be relied upon to feed regularly under all conditions. A lubricator which meets these conditions fairly well is that designed by Ottewell.[1]

Ottewell's Sight-feed Lubricator. — The valve A (fig. 139) can be opened so as to allow steam to enter from a current which passes from the boiler to the steam pipe through a T-piece screwed to the nipple H. The steam, condensing in G, fills the whole of the lubricator with water, except the lower chamber R, which contains the lubricant. The valve A, being left slightly open, allows the water in G to flow slowly into the steam pipe, and steam to enter the chamber to make good the deficiency, in the same way as the valve does in Roscoe's lubricator. When it is desired to feed oil, the valve C is opened. Oil drops, rising through the glass tube, enter the chamber G, and, with the escaping water, pass by the plug valve A. As the oil passes away, water descends through T and rises in R.

This lubricator has been found to work well on locomotive engines. For stationary engine work, however, it has been found advisable to make some slight alterations.

The lubricator may be considered as a 'Roscoe' cut into two parts and furnished with a sight-feed device, which makes it more easy to regulate.

Deeley's Sight-feed Lubricator. — Another design[2] which will feed

[1] A. B Ottewell, Eng. Patent No. 21257 (1895).
[2] R. M. Deeley, Eng. Patent No. 7281 (1892).

regularly is shown in section in fig. 140.   The branch S is coupled up to the boiler, and the branch H to the steam-pipe a short distance
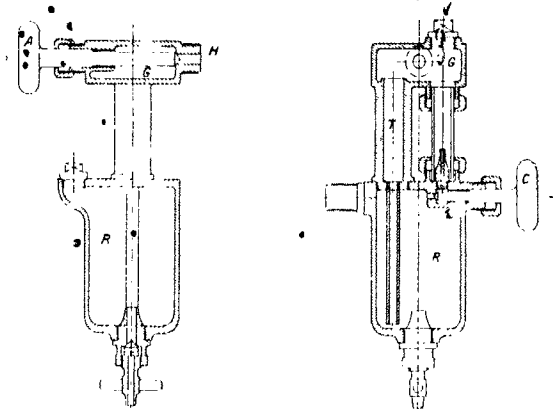
FIG. 59.
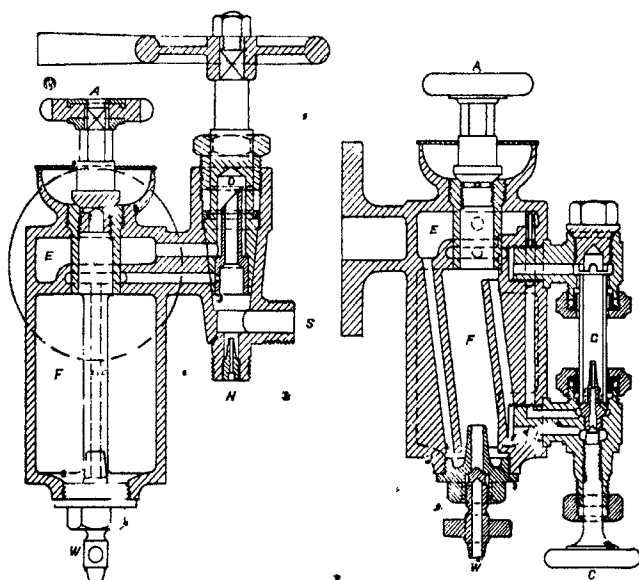
FIG. 140

from the point where it joins the cylinder steam-chest.   Through

these pipes there is a constant flow of steam, which can, however, be
stopped by closing a cock on the boiler.

To fill the lubricator, the valve D is placed in the position shown,
and steam is turned on for a time. When the lubricator has cooled
somewhat, and the reservoirs E and F and the glass tube G are full
of water, D is closed by means of a handle. Before attempting to
fill with oil, the fitting must be allowed to cool (these precautions
need only be taken when the lubricator is new and quite empty).
A is then unscrewed, and all the water that will pass away allowed
to do so by opening W. Closing W, the chamber F may then be
charged with oil. Steam having been allowed to pass through S and
H, the centre of the plug D is filled with steam at the pressure of
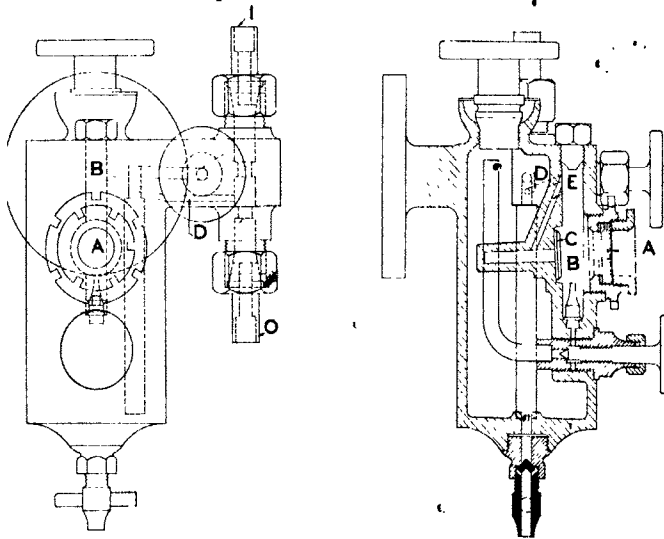
FIG. 141.

the boiler. Here it condenses, and when the upper port is open, the
water enters E, passes down the port near the glass sight-tube, and
then up the gauge glass itself. This current of hot water serves
to keep the lubricator warm—a very necessary feature when very
viscous mineral oils are used—and also to keep the glass full of clean
water. The oil can be supplied at any desired rate by opening C.
It is caused to flow mainly by the difference in the head of the two
ports in the side of the plug D, and as it escapes from the nozzle
into the water, it forms drops, which rise up the centre of the glass.
The rate of feed remains constant, however much the conditions of
running may vary. This makes the lubricator very suitable for
locomotive work.

In *Wakefield's disc sight-feed lubricator*, fig. 141, the glass tube is replaced by a thick glass disc A, through which the drops of oil can be seen rising up the tube B. Should the glass disc become broken, the check-valve C is automatically closed by steam and water pressure acting through the passage E, which enables the lubricator to continue working until the glass disc can be replaced. The drops of oil which rise up the tube B are discharged through the passage D into the pipe I O, through which a current of steam passes from the boiler to the cylinder.

There are quite a number of sight-feed lubricators in which a head of water is the motive power, and most of the arrangements are so specialized that they are only suitable for certain kinds of work.

Royle's 'Oleojector,' fig. 142, made by Messrs. W. H. Bailey & Co., acts upon a different principle.
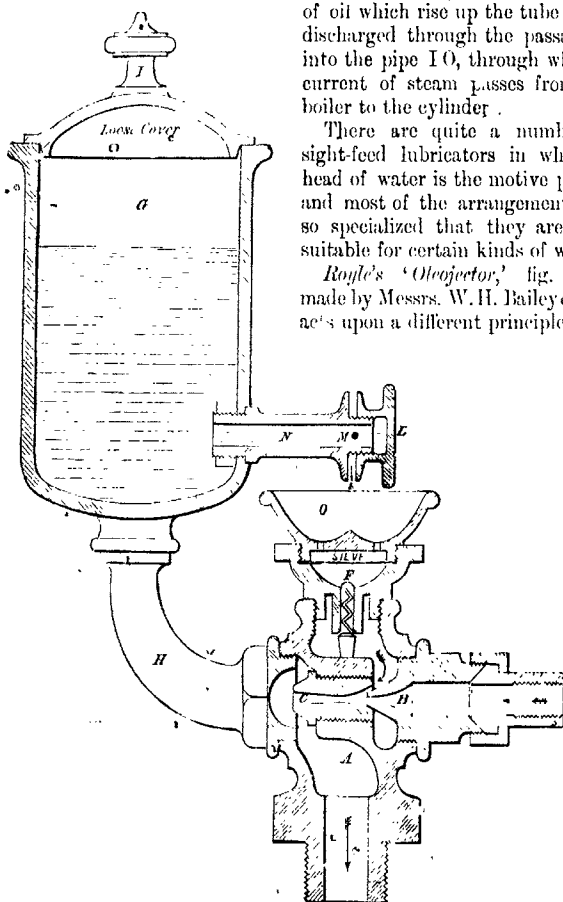
Fig. 142.

Oil from the cistern G drops into the cup O at a rate regulated by the screw valve L, and passing through the valve F is injected
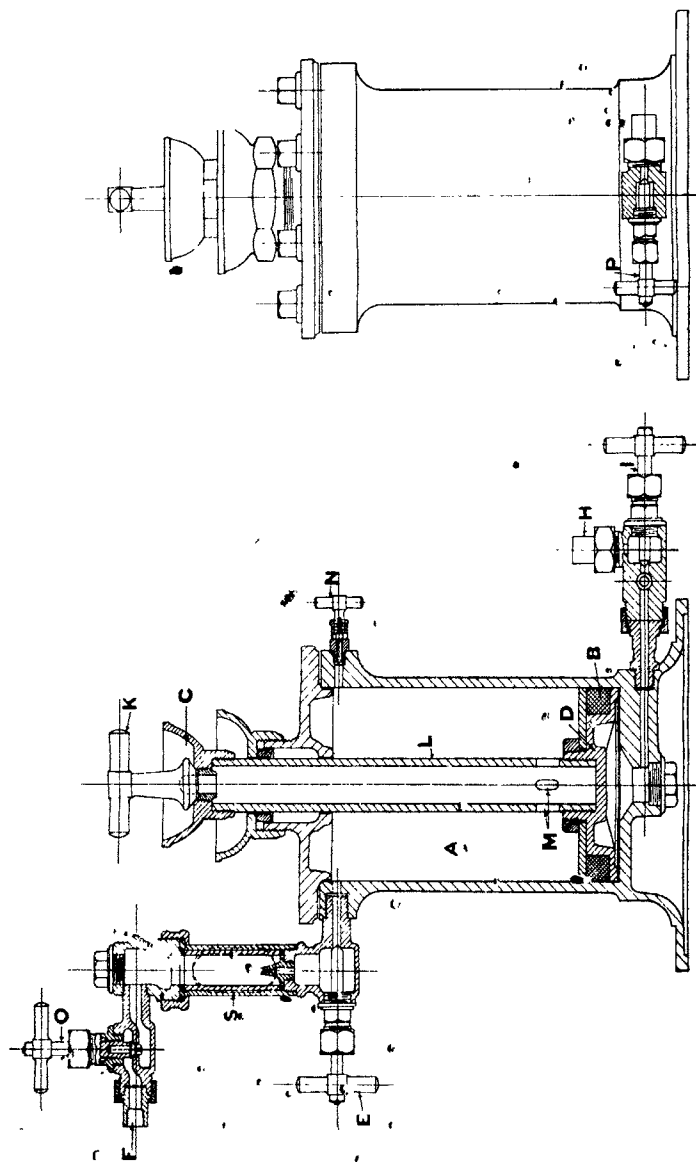
FIG. 143.—Winn's Piston Sight-feed Lubricator.

into the cylinder at each successive period of low pressure by a current of high-pressure steam from the main steam pipe which passes through the injector BCA, directly into the cylinder as shown by the arrows. At the period of high pressure in the cylinder the valve F closes and prevents the oil from returning. This lubricator must be fixed on the engine cylinder and not on the steam-pipe or valve chest. In horizontal cylinders it is best fixed in the middle, and in vertical cylinders on the top.

Winn's piston sight-feed lubricator, fig. 143, made by Messrs. Winn & Co., is a form of displacement lubricator in which the oil is supplied by the pressure of steam on a piston. It consists of a cylindrical vessel A fitted with a piston D, a hollow piston rod L, and a sight-feed arrangement S. The steam inlet is at H, and the oil outlet at F.

The piston D is packed with an asbestos ring B, held between a junk ring and the piston.

To fill the lubricator, the piston D is pushed down as far as it will go ; the plug K is removed, and oil is poured into the cup C, whence it runs down the hollow piston rod and through the holes M into the lubricator, air being allowed to escape through the plug N. After the plug K has been replaced, steam is admitted below the piston D by opening the plug I.

The amount of oil allowed to pass away is regulated by the plug E, and the number of drops passing per minute can be seen through the glass S, which is kept filled with water, the amount of oil in the lubricator being indicated by the length the piston rod projects through the stuffing box on the top of the lubricator.

The water can be drained from the part of the cylinder under the piston D, by closing the plug I and opening the plug P. By closing the plug O, the lubricator is isolated from the part being lubricated.

Fig. 143.

There are a number of cylinder lubricators, more suitable for large than for small engines, so designed that a piston, actuated by a ratchet driven from the engine cross-head, delivers at each stroke of the engine a definite quantity of oil.

The 'Rex' (*improved 'Mollerup'*) *Lubricator*, made by Messrs. Vickers & Sons, fig. 144, is one of these. It consists of a lower

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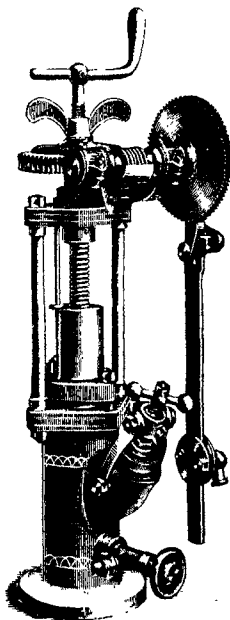
vessel to contain the oil, fitted with a hollow plunger which is actuated by an arrangement of ratchet, worm, and screw gearing.

The long ratchet arm obtains its motion by being connected to a reciprocating part of the engine; the worm wheel rotates the plunger screw when the wing nut above it is tightened, and revolves freely on the screw when the wing nut is loosened. With the worm wheel in the loose position, the plunger can be raised or lowered by turning the handle at the top of the lubricator.

To fill the lubricator, the wing nut referred to is slackened, and the plunger is drawn to the top of its stroke; the lubricator can then be filled, after removing the cap covering the large filling-hole shown at the right hand side, near the top of the oil vessel.

Friedmann's pump lubricator, fig. 145, is another of the same type. This apparatus combines in itself four lubricators, which are completely independent of one another. Each pump can be adjusted to pump various quantities of oil, and, after adjustment, the supply becomes regular, and is entirely unaffected by the counter pressure which exists in the oil pipes. Consequently, a single apparatus may be employed for lubricating at the same time cylinders under pressure, and also parts of machinery where there is no pressure.

Two eccentrics E and E', which are rotated by means of the ratchet lever L, respectively cause the self-packing pistons P and Q to move up and down. The piston P draws oil from the vessel D, which is nearly filled with oil, through O and Y, and forces it through Z, into the pressure space K. The piston Q acts as a valve, closing Y before putting Z into communication with K, and on the return stroke closing Z before putting Y again into communication with O. Thus the pressure space is never in direct communication with the oil vessel, and it is, therefore, impossible for the oil contained in it to be drawn away.

The quantity of oil which is discharged at each revolution of E depends upon the stroke of the piston P. When the regulating screw R is completely screwed down, the piston forces out its maximum quantity (about ½ gramme). If R be screwed up, the oil supply is reduced, and when screwed up as far as the pin A will permit, the discharge is at the minimum.

Each apparatus is provided with a strainer arranged under the cover W, and the several cylinders are fitted with cylindrical strainers B. A removable wire X indicates the level of the oil, which should never be allowed to fall below the level of the aperture O. The perforated plug I shows the height to which oil should be filled in the vessel. It also allows air to pass into the oil reservoir to take up the space of the oil pumped out. A drain cock M is used for emptying and draining off any water which may have got into the oil vessel.

The check valve V in connection with each pump is used to prevent steam or water of condensation from flowing back, if the filling of the oil vessel has been neglected. Steam can be passed through the passage U for the purpose of heating the oil during frosty weather.

ENLARGED VIEW OF
ONE PUMP.
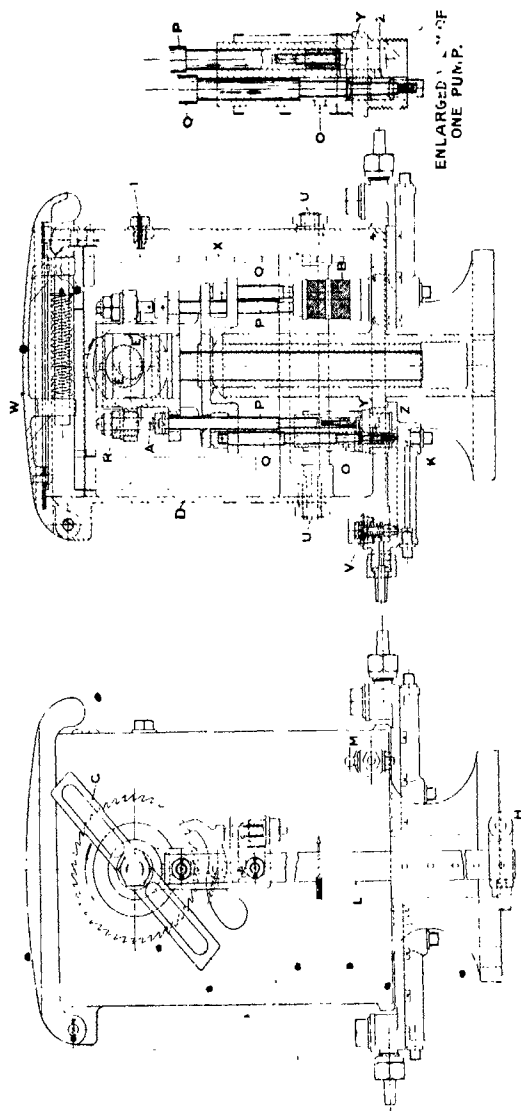
FIG. 145.—Friedmann's Pump Lubricator for Locomotives

The pumps are operated by connecting the lever L with the reciprocating part of the locomotive, and it will be seen that the stroke can be increased or reduced by altering the position of the sliding piece M. The part G is rigidly connected to the ratchet
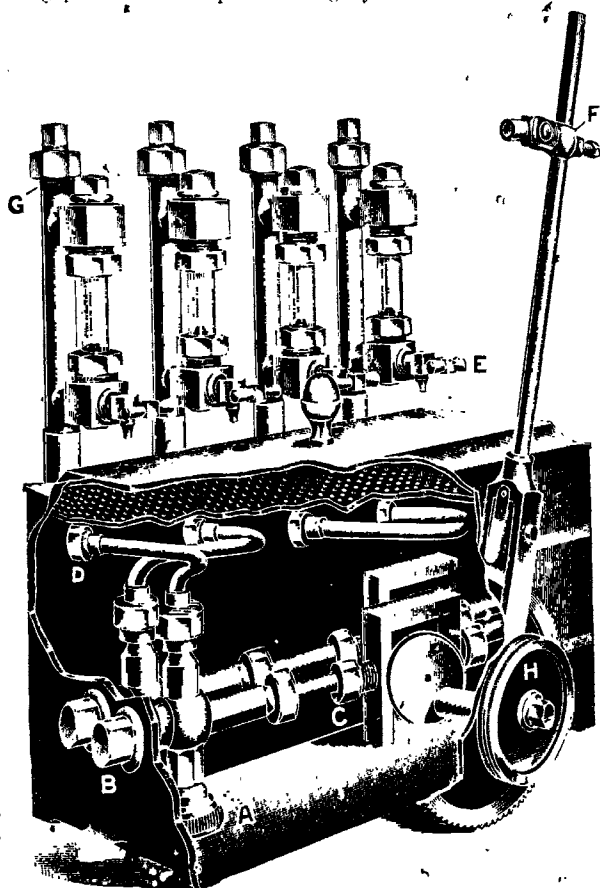
FIG. 146.

wheel, to which a handle can be fitted for the purpose of working the pump and filling the oil pipes as required.

Still another pump lubricator, made by the 'Steam Cylinder Lubricator Co. of Manchester, and known as the *Adams & Grandison sight-feed lubricator*, is shown in fig. 146.

This lubricator comprises a tank, A, containing the oil, in which are several plunger pumps, one for each feed. The supply of oil can be regulated by the taps E, the surplus oil passing back into the tank through the holes seen below each tap. The lever F is usually coupled to some *reciprocating part of the engine, but in the case of* high-speed engines a special gear is fitted for driving by a small band from some revolving part of the engine. The pumps can be worked, if required, by the hand-wheel H, for flushing purposes at starting, etc.

Chapman's patent automatic cylinder lubricator, manufactured by Messrs. Knowles & Wollaston of London, has been designed for feeding mixtures of cylinder oil and graphite, especially for high steam pressures and superheated steam. This lubricator is provided with internal mechanism, actuated by some part of the engine, so constructed that the lubricant is kept continually stirred, and, therefore, uniformly mixed from the moment it is poured into the body of the lubricator until it reaches the non-return valve through which it enters the steam pipe, thus obviating the difficulty which has been experienced in the past in feeding a mixture of oil and graphite to engine cylinders, owing to the graphite settling whenever it has a chance of so doing and choking the lubricator and its connections.

In the case of locomotives, the steam has often to be shut off and the engine allowed to run for long distances without steam. When working in this condition, there is often too little steam passing through the lubricator to more than partially lubricate the engine parts. To prevent any serious injury to the rubbing surfaces under such conditions, lubricators are placed on the cylinders. The most commonly used design is known as the *Furness* [1] *lubricator*, a section of which is shown in fig. 147. Oil is placed in the bell-shaped chamber, from whence it feeds through the wick and wire gauze cup into the central passage, which it fills. So long as the steam pressure remains in the cylinders, the small valve shown remains closed, but immediately steam is shut off, a vacuum is

FIG. 147.

formed, the valve is drawn off its seat, a charge of oil enters the cylinder, and so long as the steam remains off, the oil is slowly fed.
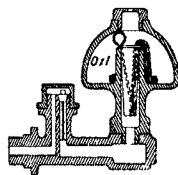
A weak feature of this lubricator is that, depending as it does upon the lifting power of wicks, it cannot be used for thick cylinder oils, unless it be steam-jacketed so as to keep the oil warm.

An *improved cylinder lubricator* of this type is shown in fig. 148. The lubricator is filled with oil through the cap W, after removing the cork L, and no oil can pass away from the container so long as the valve A is kept pressed against its seating by the spring B, as shown in the figure.

To operate the lubricator, the valve A is lifted and rotated through

[1] H. D. Furness, Eng. Patent No. 2437 (1871).

90° so that the knife edge K at the top of the valve spindle rests in the cross grooves made in the nut C to receive it. The amount of
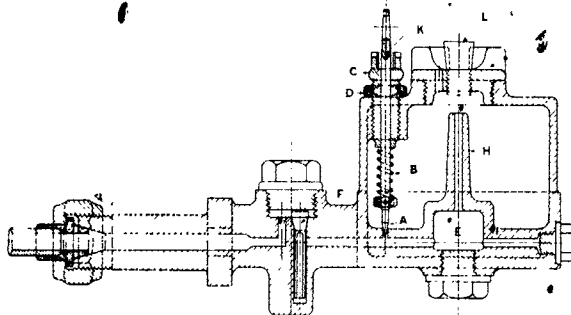
FIG. 148.

opening of the valve is regulated by raising or lowering the nut C,

FIG. 149.

until the required quantity of oil can pass slowly into the chamber E, and, when the desired opening has been obtained, C is locked by means of the nut D.
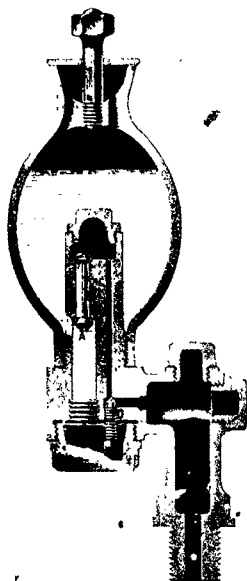
When the engine is working under steam, the valve F is kept pressed against its seating, and steam is thus prevented from passing from the cylinder into the lubricator. During this time, oil passes slowly from the containing vessel through the valve A into the chamber E, and when steam is shut off, the action of the engine piston moving to and fro creates a vacuum behind the valve F, which lifts, and oil out of E is forced into the cylinder by the pressure of the atmosphere passing down through the tube H.

The Luard automatic lubricator, fig. 149, made by Messrs. Holden & Brooke of Manchester, also dispenses with the trimming.

At each stroke (when steam is shut off) the vacuum in the cylinder causes the valve A to close and the valve A′ to open, a small fixed quantity of oil being drawn up past the three-sided spindle B at the same time. A screw C is provided in case the use of a different quality of oil

renders regulation desirable. The screw is protected by the cap D, and cannot be tampered with unless D is unscrewed.

To secure lubrication whilst the steam is shut off, the stream of oil and steam coming from the sight-feed lubricator is, in Smith's design, reinforced by a jet of steam, which, by an air-valve, is caused to flow direct from the boiler and open the steam-valve when there is a vacuum in the steam-chest.

Smith's automatic vacuum-destroying valve lubricator for locomotives, fig. 150, is used in connection with locomotive steam-
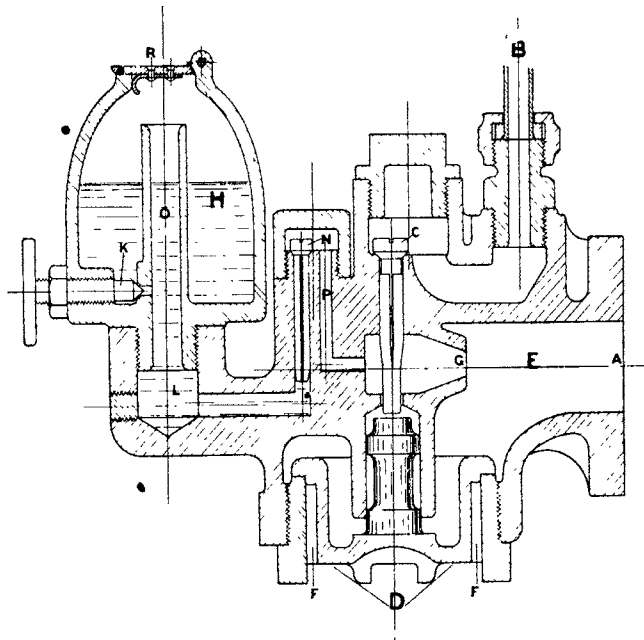
Fig. 150.--Smith's Automatic Vacuum-destroying Valve Lubricator for Locomotive Engines.

chests and cylinders, for destroying the vacuum created by the pumping action of the pistons when the engine is running with steam shut off, and for lubricating the working faces of the valves and pistons by means of a combined jet of steam, air, and oil.

The opening A communicates with the cylinder steam-chests, and the pipe B with the steam dome of the boiler. When closed, the valve C prevents the passage of steam from the boiler, through the pipe B, into the chamber E. The valve D is exposed on its upper side to the pressure of the steam in the steam-chests and

the chamber E, and on its under-side to the pressure of the atmosphere. The positions of the valves C and D as illustrated are those which obtain : (*a*) when the engine is running with the steam regulator open, and (*b*) when the engine is at rest with the steam regulator closed. When the engine is moving with steam shut off, the action of the engine pistons creates a partial vacuum in the steam-chests and in the chamber E, and the greater pressure of the atmosphere on the under side of the valve D causes it to rise and come in contact with the end of the valve C, which is lifted and allows steam to pass through the nozzle G, into the chamber E, thence into the steam-chests and cylinders ; at the same time air is allowed to pass up the passage F F, past the seating of the valve D, and to mix with the steam.

The vessel H contains a supply of oil, and the valve K regulates the amount which passes from H into the chamber L, the non-return valve N preventing the passage of steam from the steam-chest into L and H. When the engine is running with steam shut off and a partial vacuum is thus produced on the top of the valve N, the air at atmospheric pressure, which is free to enter H, lifts the valve N, and the oil out of L is forced down the passage P and is carried forward to the cylinders by the steam passing through the nozzle G.

When the engine comes to rest and the pressure in the chamber E becomes equal to that of the atmosphere, the valves D, C, and N automatically close.

The tube O is made of a large bore so that, in the event of the valve N temporarily sticking, steam will be allowed to escape freely by raising the lid R, and without blowing the oil out of H.

Design of Cylinders.—To secure good cylinder and valve lubrication, it is essential that attention be paid to the conditions which determine whether the oil shall reach the surfaces or not. The greatest enemy to good cylinder lubrication is water. It wets the surfaces where there is any abrasive action, and effectually keeps of the oil. Water may be present in undue quantity, either because i is brought into the steam-chest and cylinder from the steam-pipe, or is unable to escape from the cylinders owing to the positions in which the steam-ports are placed. When water comes from the steam-pipe in any quantity, a separator should be used and the steam dried This is nearly always done in the case of high-speed engines, such as the Willans engine. To ensure the escape of such water as condenses in the cylinders, the ports should be placed below them, or so low a one side or sides that all the water may drain away with each opening of the exhaust port. Proper drain pipes must also be fixed to the lowest points of the exhaust pipe where it rises to any height, or the water will remain in the pipe, to a sufficient extent to keep the cylinders in a wet condition and so prevent proper lubrication. To get rid of such water as is condensed in the cylinders and cannot get away freely through the main valves, Holt's drain valve has been

found very efficient. A section of this valve is shown in fig. 151.
Here the two valves, which slide freely on a spindle, so control the
movements of each other that the one
having the greatest steam pressure upon
it remains shut and holds the other open.
This results in the closing of the drain
valve at that end of the cylinder receiving
steam, whilst the valve controlling the
drain pipes at the end of the cylinder
which is being exhausted remains open.
Provided that the drain valve is not too
large for the cylinders, the water is drained
with very little loss of steam, and the
bottom of the cylinder, which in horizontal
engines has to carry the weight of the piston, remains well
lubricated.
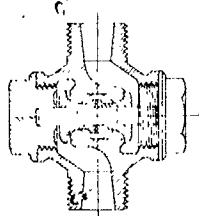
Fig. 151.

CHAPTER XI.

Genuineness of Lubricants. – The engineer in charge of a works, factory, or mill, the engineman in charge of a steam, gas or oil engine, or even the possessor of a cycle or motor car, although deeply interested in the genuineness and nature of the lubricants he uses, has, as a rule, very limited means at his disposal for determining the nature of the oils, greases, etc., which he purchases. It is no doubt to this state of things that we must attribute the very extensive use of adulterants by manufacturers of lubricants, and the placing upon the market of improperly or imperfectly refined oils.

Makers of sewing and other small machines generally themselves sell the kind of oil most suitable for their lubrication. Such firms are able to obtain a genuine article, and it would be contrary to their interests to allow their customers to use an unsuitable oil. The retail prices charged for such machine oils are, however, so high as to be prohibitive where lubricants have to be used in large quantities and it is then necessary to purchase from a wholesale dealer, and to take proper precautions to ensure that the lubricant is free from adulterants and suitable for the bearings upon which it is to be used.

The most valuable and expensive oils, such as sperm, olive and lard are extensively adulterated with cheaper fixed oils and with mineral oil Cottonseed oil is frequently mixed with olive and lard oils, and is sometimes almost wholly substituted for the former. Much of the olive oil sold for lubricating, if not adulterated, contains so much free oleic acid as to be quite unfit for use. Indeed, many lubricants are mixtures of various liquids or soft solids, some of which are very injurious. Adulteration, with a view to the thickening of the lubricant, is mainly resorted to in the case of mineral oils; these are also adulterated with rosin oil, and occasionally with neutral coal-tar oil. The sophistication is often very skilfully done, the problem being to add such cheaper ingredients to the more expensive oils as will enable them to pass as many of the tests of the chemist as possible. Attempts are sometimes made to thicken the thinner burning or intermediate petroleum oils, so as to make lubricants of

them. It thus appears that unless the purchaser has some means of ascertaining the true character of the lubricant he is using, he has little or no guarantee of its genuineness or fitness for use.

A great improvement has been made of late years in the quality of mineral lubricating oils. By improved methods of refining, less destructive distillation takes place, and the lighter fractions are more perfectly separated from the heavier ones, thus making the various grades more homogeneous in their composition.

Simple Tests for Adulterants and Impurities.—In the majority of instances, the engineer in charge of a small station has no means of obtaining an accurate knowledge of the true character of the oils supplied to him, other than by consulting an analytical chemist versed in the methods of examining lubricants, for many of the adulterants used require careful analysis to even detect their presence. In Chapters VI. and VII. the most important of the chemical and physical methods in use for the detection of adulterants have been described in full. Most of these can only be practised by a skilled analyst in a properly equipped laboratory. Some of the tests, however, can be made with very simple apparatus, and these the engineer should make himself acquainted with, as they will furnish some very valuable information concerning the purity and properties of the lubricants offered to him. The very important test for free acid is one of these (p. 215). A rough but very useful test can be made in a stoppered 50 c.c. graduated test mixer, into which 15·4 c.c. (=about 14·1 grms.) of the oil are carefully measured. The cylinder is filled up to the mark with neutralised methylated spirit, some phenolphthalein solution is added, and normal caustic soda is dropped in from a burette, until, on shaking well, the pink colour is permanent. The number of c.c. of caustic soda used, multiplied by 2, expresses, approximately, the percentage of free (oleic) acid in the oil. All the solutions, the test mixer, and the burette and stand, can be purchased for a few shillings from any dealer in chemical apparatus. Dipping blue litmus paper into the oil, as frequently recommended, is a useless test. Another easily made and very valuable test is the watch-glass test for gumming properties (p. 265). The oil can be carefully measured instead of being weighed, and it compared under *exactly the same conditions* with a standard sample of oil, useful information may be gained   The watch-glasses can be placed side by side in any suitable hot situation protected from dust, and thus even the hot air or water-oven can be dispensed with. In many cases it is not worth the trouble and time to ascertain the exact nature of the adulterant used, the tests being merely such as will indicate whether the sample examined is fit for use.

Such tests considered in the light of the results obtained with his machinery will enable the engineer in most cases to detect the cause of any irregularity in working. When the quantity of oil, grease, etc., used is large, it becomes necessary to have analyses of the lubricants supplied regularly made by a competent analyst, in order

to make sure that they are suitable for the purposes required, and are equal in quality to the sample offered, or that they comply with the specification. (See Chapter VII., pp. 210 306.)

Qualities and Properties of Lubricants. — *Acidity.* — Although animal and vegetable lubricants differ from mineral lubricants in their chemical constitution and activities, in many of their physical properties they closely resemble each other, and it is to these common properties that they owe their lubricating values. Of these properties, viscosity and oiliness are the most valuable. But it frequently happens that an oil, which would otherwise be a good lubricant, fails to be of practical use owing to its having been allowed to become acid, or to its property of taking up oxygen from the air and becoming thick, either evaporating entirely at ordinary temperatures or leaving a gummy, sticky mass behind. These properties have been dealt with in detail in previous chapters, and need only be referred to here in so far as they concern the use to which the lubricants may be put.

Oxidation and Gumming. - Many oils when exposed to the atmosphere as thin films on bearings rapidly thicken by oxidation, and finally form gum or varnish like masses, which clog the moving parts and cease to act as lubricants. A high temperature considerably hastens the rapidity with which this takes place. Gumming oils, such as rape, should not on this account be used in warm places, as they rapidly become thick, clog the trimmings, and considerably reduce the speed of flow through them to the rubbing surfaces.

In places where animal or vegetable oils which are liable to gum have to be used, great care must be taken to prevent the accumulation of waste or other fibrous material saturated with them from being placed near steam pipes, or stored in closed cupboards. Such material should be kept in iron bins in the open air, for in the process of oxidation or slow burning which accompanies gumming, heat is evolved in such quantity as often to set fire to the whole mass. Mineral lubricating oils of high flashing-point (not below 340° F.) which are devoid of this property, should be used in theatres, hotels, and other large buildings where the risks of fire are great, either alone or mixed with fatty oils which gum only slightly (see p. 278).

To clean machines which have become covered with a gummy oxidized lubricant, the parts should be well moistened with paraffin oil, which dissolves the gum, allowed to run for a few minutes, and then wiped dry and clean before being oiled again.

An old-fashioned test, now superseded in the laboratory, is that of Nasmyth. A plate of iron or steel 6 feet long by 4 inches wide, has six longitudinal grooves planed in the upper side. It is placed upon a bench or shelf, in a warm situation as free as possible from dust, slightly inclined, one end being supported on a block 1 inch thick. An equal number of drops, measured from the same pipette, of each oil to be tested and of a standard sample, are placed successively in one of the grooves, and the behaviour of the different

oils is observed from day to day. Those of least viscosity will, at first, flow most rapidly down the incline, but oxidation or any other cause tending to thicken the oil will gradually arrest its motion, and the effect after a few days will become marked, the best oil flowing the greatest distance.

All animal and vegetable oils, fats, etc., contain acid constituents which will attack the metallic surfaces of bearings and form soaps of iron, copper, etc. The tendency they have to become more acid with age is very slight in most cases, if the oils are properly refined and not stored too long. The extent to which lubricants may be expected to contain acid constituents, and the best methods for their detection, will be found in Chapter VII., p. 210.

The temperature at which an oil flashes when a light is brought near its free surface is called the *flashing-point*. This property has been fully discussed in Chapter VI., p. 186. No lubricating oil which flashes below a temperature of 340° F. should be used for indoor machinery without special precautions being taken to prevent risk of fire.

Freezing.—Many oils, which at ordinary temperatures are clear, transparent liquids, become, if the temperature falls sufficiently low, white, opaque, solid masses. Sometimes, as has been shown in previous chapters, the whole mass of the liquid solidifies at some particular temperature, or certain constituents are thrown down as precipitates ; whilst in other cases, as the temperature falls, the liquid becomes more and more viscous, and finally becomes a soft solid. This must be borne in mind whenever bearings are exposed to cold. In such cases the reservoir in which the oil is stored, and the trimmings or other arrangement for supplying the oil in a regulated stream, must be placed close to the shaft, so that the heat resulting from a deficiency in the supply of the lubricant may cause it to flow again, i., by chance, an oil which easily solidifies should be used.

Oiliness.—When a grease is rubbed between the fingers it will be found that they slide freely over one another even when pressed together with considerable force. A similar effect is produced when a greasy finger is rubbed over a sheet of glass or other smooth solid. This arises in great measure, if not wholly, from the fact that the grease is not a liquid or viscous substance, but a plastic or very soft solid, which cannot by pressure alone be wholly driven from between the surfaces. On the other hand, the soft solid is easily shed, the resistance offered to the sliding of particle over particle being very small. This property of greases causes them to form very thick lubricating films, even when the loads are heavy and the speeds moderate. At higher speeds, however, they do not compare favourably with the oils, the frictional resistances being much greater.

Except for special bearings, greases are now giving way to blended oils, for the high coefficient of friction and resulting loss of engine power is by no means compensated for by the decreased cost of the lubricant.

Greases are generally made by thickening a mineral oil, fixed oil or fat, with a soap of lime, soda, lead, etc., more or less water being emulsified with the oil and soap. In some cases solids, such as black-lead, French chalk, and mica, are also added. A number of these lubricating greases are described in Chapter V., p. 126, et seq. They are liable to be adulterated with excess of water, and with solids such as china clay and gypsum, which are not lubricants.

The corresponding property in the case of liquids, which prevents the lubricant from being easily pressed out, is called oiliness. Different liquids possess this property in very different degrees. Thus, although sperm oil is much less viscous than glycerine, it will be found to be a much better lubricant. The glycerine feels harsh between the fingers, whilst the sperm oil feels smooth and greasy. The viscosity of an oil, therefore, by no means furnishes us with an index of its lubricating value. With high speeds, moderate loads, and good lubrication, it is no doubt the degree of fluidity which principally determines the value of a lubricant for any particular purpose; but when the speeds are slow or very high, the loads great, or the lubrication imperfect, oiliness as well as viscosity play an important part in the reduction of frictional resistances. (See Chapter III., on 'Superficial Tension.')

The property of oiliness is generally possessed most markedly by the animal oils, less so by those of vegetable origin, and least of all by some mineral oils. It is on this account that fixed oils are so frequently added to mineral oils, for they give to the latter just that property in which the mineral oils are most deficient.

No simple laboratory test has yet been devised for ascertaining the comparative *oiliness*, or carrying power under heavy loads and at low speeds, of lubricants. Such information is generally obtained by means of mechanical oil-testing machines. However, the value of the results they give, considered from this point of view, varies with the speed, load, and method of oiling adopted—matters which are as fully discussed in Chapter IX., on the 'Mechanical Testing of Lubricants,' as our present knowledge seems to warrant.

Viscosity.—Upon the viscosity or degree of fluidity of the lubricant depends the resistance which it offers to the motion of the rubbing surfaces of quick-running machinery, and also, in some measure, the loads which bearings will carry at ordinary speeds without suffering abrasion. Each particular animal or vegetable oil has a viscosity which does not vary greatly in different samples, and may be regarded as being in some measure an indication of its purity or genuineness. The viscosity of such oils, therefore, need not be specified when ordering, but should be determined for the purpose of ascertaining probable purity. Mineral oils, however, having a great range of viscosities may be purchased, and it is necessary to state in all cases the degree of fluidity required.

The viscosities of all lubricants vary very considerably with changes of temperature. Thus an oil which, as long as the journal runs cool,

is sufficiently viscous to carry the load properly, may become so fluid, if the temperature should rise from any cause, that the rubbing surfaces close together and cut and car each other. The variability of the viscosity of a lubricant with change of temperature is often so great that an oil which works well in a cool place may be altogether too 'thin' for a hot engine-room or warm climate. Castor oil, whilst too thick for locomotive bearings in England, is, on the other hand, largely used in India, where it answers well. Mineral oils vary more in viscosity with change of temperature than do fixed oils. On this account the changes of a bearing lubricated with a non-fatty oil going from bad to worse are great, and needs more careful attention.

The nature and measurement of this property are fully dealt with in Chapters II. and VI.

Staining of Fabrics. The lubricants used for the bearings of textile machinery are liable to be thrown about by the rapid motion of the spindles, shafts, etc., and falling upon the cotton or woollen goods, produce more or less objectionable stains. Every care is, of course, taken to prevent this splashing of the lubricant, but as it cannot be altogether prevented, and is apt to spoil the appearance and reduce the market value of the cloth, care is taken to use only lubricants which either stain very little or give stains which are easily removed. Pure mineral oils, it would appear, all produce objection able stains which can with difficulty be wholly removed, for they sink into the fibre and carry with them the fine metallic powders ground off the bearings. On this account, even though the oil be clean and colourless before use, and be apparently completely removed in the scouring, the chemical changes which the metallic powders undergo sooner or later, sometimes months later, produce stains of various colours in the finished goods. Stains produced by the oil thrown from heated bearings are found exceptionally difficult to remove, especially if the stained goods have lain in stock for two or three months. When such goods are bleached, the fabric is often found to have become rotten, and a hole makes its appearance where the stain had been.

Animal and vegetable oils are much less liable to produce permanent stains, for, being saponifiable, they are almost wholly removed if the various dressing processes the fabric has subsequently to undergo. With them may be mixed from 25 per cent. to 30 per cent. of mineral oil without producing any marked effect upon their staining qualities. In greater proportions, however, the results are not satisfactory.

The colour of these stains depends upon the metals of which the rubbing surfaces are made. Iron produces a red stain, whilst copper or brass stains are grey, greenish, or black.

One of the most usual, as well as one of the most effective, methods of dealing with mineral oil stains in cotton goods is to impregnate them with olive oil or oleine (crude oleic acid), allow half an hour for the oil to thoroughly permeate the stained part, and then

boil the goods in a caustic soda lye for six or eight hours.   Olive oil is more efficacious than oleine ; and if, before boiling, the fabric is well scoured with soap and a little carbonated alkali, the mineral oil stains are more thoroughly and easily removed than when boiled in the kier at once. In the case of dyed and finished fabrics which cannot be wetted again, benzine or benzoline, which dissolve the mineral oil, can be used.[1]   The solvent should be applied first in a ring all round the spot, and gradually brought nearer to the centre, and a fibrous substance, such as blotting-paper, used to absorb the oily solution which is driven to the centre.   If the solvent be applied to the oily spot direct, the grease is caused to spread into the fabric.

Blended Lubricants. — *Mixed or Blended Oils.* — Mineral oils being much cheaper than the better class of fixed oils, and as, at the same time, they possess valuable properties which they confer upon other lubricants with which they are mixed, the use of blended oils has now become common. Indeed, quite apart from the pecuniary aspect of the case, the blended oils are for many purposes superior to either pure fixed oils or pure mineral oils   The percentage of mineral oil permissible varies according to the load, speed, etc., for, unfortunately, many, if not all, mineral liquid lubricants are deficient in the property we have called *oiliness*, and can seldom be used quite pure, except in those cases (bath, ring, or forced lubrication) where the journal and bearing are kept flooded with oil.   At one time mineral oils were regarded with great distrust both by chemists and engineers, and when found mixed with fixed oils they were regarded as objectionable adulterants.   The reverse now seems to be the view often taken, fixed oils being sometimes looked upon as adulterants when found mixed with mineral oils.   This view seems to have arisen from a conviction that the lubricating value of an oil is wholly due to its viscosity, and that as mineral oils can be prepared of any desired viscosity, fixed oils could be wholly dispensed with.   Oils were consequently placed upon the market which were stated to be free from fixed oils, and were sold as pure mineral oils. They, however, proved on analysis to contain a proportion of fixed oil—in other words, they were really blended oils.

In the majority of instances these mixed oils answered admirably, a fact which served to strengthen the view that, from a frictional point of view, viscosity was the property which determined the value of an oil.   But chemical analysis was not slow in proving that these so-called pure mineral oils really contained fixed oils, and that it was largely owing to the presence of these fatty constituents that the good results obtained in practice were due.   More rational views are now coming into vogue, and users of lubricants are beginning to recognize the fact that the best lubricants for most purposes are obtained by the careful blending of animal and vegetable oils, fats, or waxes with mineral oils.   Pure mineral oils are, however, used with quite satisfactory results for forced lubrication, and they must

[1] Pentecost, *Jour. Soc. Chem. Ind.*, 1897, p. 409.

be used for lubricating the cylinders of condensing engines and for swabbing the piston rods of marine engines, otherwise fixed oils would be liable to find their way into the boilers and cause leakage.

The following broad principles can, in the absence of more accurate knowledge, be laid down

Fixed oils, if of sufficient viscosity, and fats, act best at great pressures, mineral oils at light pressures. On the other hand, viscid oils give the best results at low speeds, and thin oils at high speeds,[1] though the viscosity at low speeds must not be greater than is necessary, otherwise the friction is increased.

Pure mineral oils are suitable for pressures below 70 lbs. per square inch with free lubrication, and when the metals in contact are such as do not readily seize each other. With increasing loads the proportion of fixed oil which it is desirable to add must also increase, if satisfactory results are to be obtained as regards friction and wear. By raising the viscosity beyond what is required to carry the load, instead of adding a fixed oil, the friction is sure to be increased, even though the rate of wear of the rubbing surfaces may be reduced, and more power is wasted than the economy in fixed oil warrants.

From the chemical point of view there are good reasons for mixing as large a proportion of mineral oil with any fixed oil as will not interfere seriously with its load-carrying properties. By such admixture, the tendency to gum is much checked, the oil remains fluid, and cotton waste saturated with it is much less liable to fire spontaneously.

As bearing upon the changes which take place in blended oils when used over and over again for long periods, the following results may here be given. The oil in the first column, marked 'new,' was a blended oil used to lubricate the 'blower' of the Thomson-Houston dynamo. The same oil was used to lubricate the armature bearings. The oil in the second column, marked 'old,' was some of the same oil which had been used for the latter purpose, filtered, and used again, for a period of six months.

	New.	Old.	Rape Oil.
Relative viscosity at 60° F.,	308	315	410
Relative viscosity at 100° F.,	98	100	158
Specific gravity at 60° F.,	0·9026	0·9030	...
Total fatty acids,	5·83%	6·82%	...
Free fatty acid,	0·28%	0·42%	...
Difference ; equivalent to neutral fatty oil,	5·84%	6·53%	...
Mineral oil.	94·16	93·27	...

The above results show that by continued use there had been a loss (probably by evaporation) of mineral oil, and a consequent increase in the percentage of fatty oil. This change had resulted in a slight increase of viscosity and of specific gravity. The fatty oil had undergone some oxidation, resulting in a lowering of the melting-

[1] Any pressure below 70 lbs. per square inch may be regarded as a light load, and any speed below 100 feet per minute as a low speed.

point of the fatty acids and a darkening of the colour, also a slight, but only very slight, increase in the percentage of free fatty acid.

Animal and vegetable oils cannot, however, be added to all mineral oils with impunity. Solid hydrocarbons are present in some mineral oils, which, when they are mixed with vegetable oils, separate out as a precipitate and cause trouble by clogging trimmings, valves, etc.

We have seen that much is to be gained both in economy and efficiency by mixing in suitable proportions mineral oils with fixed oils. Quite a number of these blended oils are placed upon the market, many of them being sold at fancy prices. It is better, therefore, for the large consumer to purchase the pure lubricants he requires, and to blend them himself to suit the conditions under which they are to be used.

Fats and Greases.—The contrast in lubricating properties between mineral and fixed oils exists equally in the case of a pure mineral grease like vaseline and an animal fat such as tallow, the latter possessing in a far greater degree the property of greasiness. In the case of purified vaseline this is due partly to the fact that the excessive refining tends to remove those constituents of the crude oil upon which the lubricating property depends. Thus some of the best mineral cylinder oils, which are excellent lubricants, are obtained from the same crude oil as vaseline.

A large number of lubricating greases are made by incorporating or emulsifying animal and vegetable fats with soap and water, also by thickening mineral lubricating oils with soap. Some of these are described in Chapter V., p. 126. Large quantities of these greases are used, with very good results, for the lubrication of railway wagon axles, and some of them are excellent lubricants for the bearings of slow-moving machinery. When the loads to be carried are exceptionally heavy, solids, such as plumbago and soapstone, are sometimes added to the grease. These solids prevent abrasion at points where the pressure forcing the surfaces together is very great.

Except in special cases, greases should not be used for quick-running journals, shafts, or spindles, the frictional resistance which they offer to the relative motion of the surfaces causing great loss of power. Thus a case is mentioned by Simpson in which the owner of a mill using water power decided to use grease as a lubricant instead of oil, but owing to the increased friction, the change in the method of lubrication caused the water power to be insufficient to drive the machinery, and the use of oil had to be reverted to. Woodbury used oil for one of the two rows of looms in a cotton mill, and a consistent fat for the other. He found, under the same running conditions, that the temperature of the bearings lubricated with oil was only 4° higher than the temperature of the room, whereas the temperature of the other bearings was 22° higher. With soap-thickened mineral oils there is the liability of separation taking place, especially under the influence of steam or moisture. The mineral

oil may run away and leave the soap in the grease-box or on the bearing, which is apt to run hot in consequence.

In the case of fats and greases whose melting-point are not much above the temperature of surrounding objects, it generally happens that the lubricating films are so warmed by the friction of the bearings that they actually melt when drawn between the rubbing surfaces and act as oils.

Although unsuitable, on the whole, for moderately quick-running machinery, greases answer admirably in cases where the speeds are low, or where a low coefficient of friction at starting is essential. The cheaper greases, made with rosin oil and lime, are used for cart and truck axles whilst those composed of lubricants of superior quality are used for railway wagons, pedestals, etc.

Being soft solids, special methods (see pp. 417 and 436) have to be provided for their application to the bearings, for they do not liquefy so long as they are kept moderately cool. For railway vehicles, only the better classes of greases are used, and as friction is an important consideration, the ingredients are in some countries changed to suit the seasons, for a grease sufficiently thick for summer might be altogether too stiff for winter temperatures (see p. 128).

It is well to bear in mind that it is only when the speed of rubbing is low that economy results from the use of greases. At all ordinary velocities a marked increase in the friction is brought about by them. This loss of power is seldom estimated at its true value. As a matter of fact, it may greatly exceed the gain resulting from the use of the cheaper lubricant.

In the United States, recently, very satisfactory results have been obtained by the use of grease for locomotive lubrication. In a preliminary report made by a Committee of the American Master Mechanics' Association (see *Mechanical Engineer*, 28th July 1906) it is stated that during four years' experience with 203 locomotives fully equipped for grease lubrication during the whole or part of that time, the lubrication of pins and driving axles with grease has proved less costly than with oil. There has also been a decided decrease in engine failures due to hot bearings. Journals lubricated with grease have been found less liable to be cut, and, therefore, have required less frequent turning up in the lathe. It is pointed out that grease lubrication as applied to driving boxes is practically automatic, and is, therefore, more independent of neglect on the part of the driver than is oil lubrication. As regards the increased frictional resistance due to the use of grease instead of oil, it is stated that it has in no case been found necessary to reduce the tonnage rating of a locomotive on account of the change from oil to grease, but no data is given as to coal consumption.

In some locomotive tests carried out by the Pennsylvania Railroad System at the Louisiana Purchase Exposition in 1904 it was found that the lubrication of locomotive axles by hard grease increased the friction losses per axle by from 75 to over 100 per cent. as compared

with oil lubrication. The grease used was composed about as follows :—

Oil, veg.	.	.	.	.	.	.	.	.	.	28·66
Soap,	.	.	.	.	.	.	.	.	.	55·3
Water,	.	.	.	.	.	.	.	.	.	15·51
										100·00

A cake of this hard grease was pressed against the axle by springs ocated in the bottom of the driving-box cellars (underkeeps), a perforated plate being used between the axle and the cake of grease.

Clarification of Lubricants.—*Oil Filters.*—Pedestals, worm-wheel cases, spindle bushes, and various other descriptions of bearings are now frequently made to hold comparatively large volumes of oil which bathes all the rubbing surfaces, and by placing dishes, into which the surplus lubricant runs, below the ordinary forms of
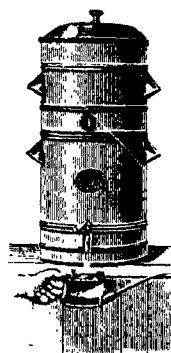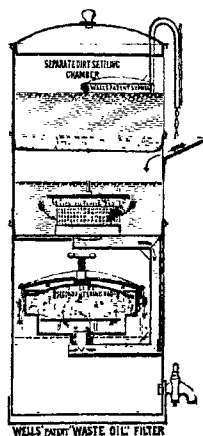
Fig. 152

bearing, a good deal of oil which was formerly lost is collected. Such oil contains finely suspended matter of various kinds, and is thick and muddy. Being, in the majority of instances, chiefly composed of mineral oil, which does not become changed in character, it is possible to filter out the suspended matter and use the oil over again, for, as a rule, the only change which has occurred is a slight increase in the viscosity, due to the evaporation of mineral oil. In this way all loss of lubricant, other than that resulting from evaporation and some unavoidable waste, is guarded against, and the greatest possible economy secured.

The suspended particles are mostly very fine, and, being immersed in a fairly thick liquid, are not easily removed.

A filter (fig. 152), made by Messrs. Wells & Co., effects this

separation of the solid matter from the oil in three stages. The muddy oil drawn from the reservoirs and contained in the oil pans is placed in an upper settling chamber, in which the heavier particles slowly subside. From this chamber the oil is drawn off by means of a siphon pipe, which floats on the surface and slowly removes the clear upper liquid, passing it into a chamber containing a filter, in the coarse mesh of which the larger suspended particles are left.
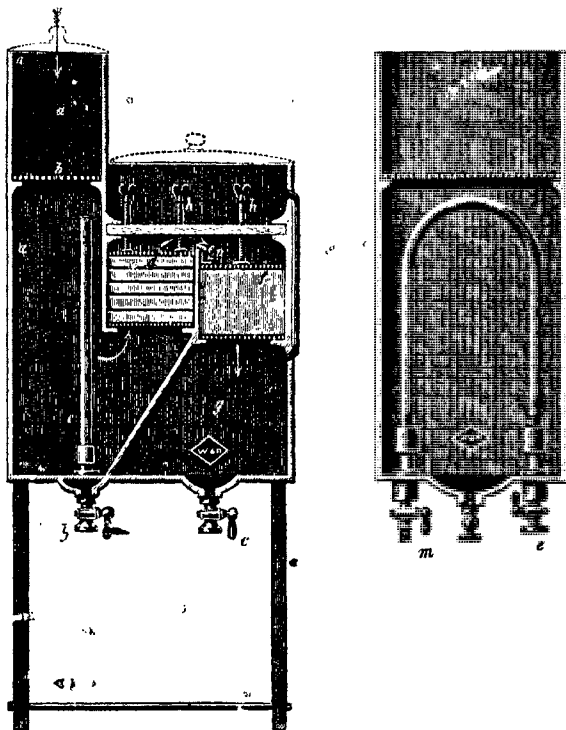
Fig. 153.

The oil finally runs into a finer filter pad, through which it is forced by a head of oil several inches or feet in height, as the case may be, and passes into a lower chamber from which it can be drawn for use. The filter pads are readily changed or cleaned.

A filter of different pattern, of which a and b are sections, is shown in fig. 153. The dirty oil is placed in the chamber a, to the bottom of which water, dirt, etc., gravitate. The oil having freed itself

from the coarsest and heaviest impurities, forces itself slowly through the chamber d, which has been filled with compressed new twist (preferably white unbleached), rises over the partition e, and then filters through the chamber f, also filled with compressed twist, into the chamber g, from which the clean oil can be drawn off through a cock. It is necessary to heat the oil to 140°–212° F., according to its consistency. This is done in the lower part of the chamber a by means of a coil c, through which steam can be passed from the engine mains as desired.

The essential features of a good oil-filter are :—

1. A capacious settling chamber, in which the oil can be warmed, if necessary to increase its fluidity, and in which water and dirt can settle out.

2. Double filtering chambers, through which the oil passes from the settling chamber (a) by upward and (b) by downward filtration. The filtering material should be the best white cotton yarn or waste, and should be capable of being compressed by means of an adjustable screw.

3. An arrangement for distributing the oil evenly over the surfaces of the filtering pads.

Evil Effects of Grit, etc.— Before rejecting any particular lubricant because difficulty has been experienced owing to the heating of the bearings supplied with it, care must always be taken to ascertain whether the fault really lies with the lubricant, or with impurities accidentally introduced. Enginemen are apt to think that a certain number of hot bearings are sure to occur, however careful they may be. No doubt, even when the greatest care is taken, bearings will occasionally run hot. But in all such cases the heating must arise from some irregularity, and the extent to which trouble is experienced is, in the majority of instances, a measure of the capacity of those in charge of the machinery to keep things in good order. Thus, as an instance, although the quality of the oil used may be excellent and very suitable for the purpose for which it is being used, still the engineman may be troubled with hot bearings, often, indeed, when extra care has been taken to keep the machinery in good order by giving it an ample supply of oil. This almost always arises from the presence in the lubricant of mechanical impurities, such as sand, sawdust, glass, vegetable fibre, mucilage, or precipitated paraffin. In transparent oils these are easily seen, but in the thicker dark varieties they are almost entirely invisible. When oil containing such impurities, which it very commonly does, is poured into oil cups in the usual way, the solids are filtered out by the trimmings, or settle to the bottom of the reservoir, and do not get into the bearings. But enginemen frequently go round their engines and pour a little oil into the ends of the bearings, or even remove the trimmings or oil-pads and pour oil directly upon the bearing surfaces, and thus introduce grit at points where it can easily get between the rubbing surfaces. Films of various kinds also settle on the trimmings, or obstruct the oil

passages, and prevent the oil from finding its way with the necessary freedom to the working surfaces.

Importance of straining all Oil.—In most engine-houses the different oils required are stored in iron tanks, from which they can be drawn as required. Into these tanks the lubricants are pumped from the barrels supplied by the oil merchants. To enable as much of the oil to be removed as is possible, the pump pipe is passed through the bung-hole and reaches to within a very small distance of the barrel bottom. The oil, as it is drawn out, thus carries with it the greater part of any solid material which may lie there. To prevent such foreign matter from passing into the oil tank, a receptacle made of fine wire gauze should be fitted into the manhole of the tank in such a manner that it can without difficulty be taken out and cleaned.

To still further reduce the risk of small particles of grit entering the oil-can, the lubricant as it is given out for use should be carefully strained through wire or cotton gauze as it is drawn from the tanks; for however good it may be, the fine solid particles it sometimes contains, if, as we have seen, they should chance to be introduced between the rubbing surfaces, will give rise to excessive friction, cause overheating, and make the engineer feel uncertain whether he is using a suitable lubricant or whether his supply is really up to sample.

When the loss which may result from the stoppage of the engines driving a large mill or ship, or generating current in an electric installation, is taken into consideration, this double precaution, adopted to prevent the introduction of solid matter, does not seem uncalled for.

Grit may also be found in solids, such as natural graphite. As such solids mixed with fats are sometimes used to put upon bearings which have suffered abrasion and become overheated, its presence may quite defeat the purpose for which the solid was applied.

Lubrication of Bearing Surfaces.—*Lubricants for Low Speeds.*—When the relative speeds of the rubbing surfaces are less than 10 feet per minute with abundant lubrication, or even greater speeds than this with siphon lubrication, the lubricant, instead of being forced between the journal and brass and parting them, is rather swept on one side, especially under high pressures; the lubricant then depends for its efficiency upon its oiliness as well as upon its viscosity. As the actual loads which bearings will carry under such conditions without seizing depend largely upon the nature of the surfaces in contact, as well as on the oil used, it is not possible to give more than very general figures. The relative carrying powers of oils, greases, and solid lubricants can, however, be approximately stated, and the engineer must in each case by actual trial select that which gives the least amount of heating and friction.

Dealing in the first instance with those lubricants which have the greatest carrying power we have—

(a) Graphite, soapstone, and other solid lubricants used dry.

Their efficacy depends largely upon the nature of the rubbing surfaces. Graphite, for instance, gives the best results when used on cast-iron surfaces, which are naturally somewhat porous. When these lubricants will not keep the bearing cool, the liberated heat must be carried away by a continuous stream of cold water passed over it or through perforations in the metal. The wear and loss of power under such conditions are very great.

(b) Solid lubricants mixed with animal fats, greases, vaseline, etc., or rosin grease. These mixtures are very suitable for heavy work, especially when metal works against wood. Rosin greases are largely used for all kinds of rough work, such as cart axles, tip wagons, hauling machinery, etc.; they give a small coefficient of friction at low speeds, do not waste away very rapidly by evaporation, and do not run off the bearings, leaving them dry.

(c) Axle greases composed entirely of animal and vegetable fats or mineral oils emulsified with water, soap, and sufficient alkali to neutralize acidity. These greases are excellent lubricants for all slowly moving shafts and journals which have to carry considerable loads. Even for railway wagons they are largely used; for the frictional resistance is small at low speeds, and trams lubricated with them are easily started. Care must, however, be taken that these greases do not contain excess of water and are not adulterated with such useless substances as china clay; also that they melt as a whole, and that the oil does not run down and leave the soap. This is liable to occur with badly made greases, and hot bearings are the result.

(d) Fixed oils, mineral oils, and mixtures of the two. In selecting oils for very low speeds and high pressures, viscosity must be the first consideration, and next to that oiliness. This is plainly shown by the experimental results in Table XCID. on p. 345. If an oil of sufficiently high viscosity be used, a mineral oil may give as good a result as, or even a better result than, a fixed oil; a mixture may give a better result than either. If an oil of sufficient viscosity be not available, then a fixed oil may be expected to give the best results.

Good antifriction metals assist greatly in reducing the friction. Goodman found cast-iron bearings lined with pure lead among the best under constant loads up to 500 lbs. per square inch and even higher. Magnolia metal has also been found to give excellent results under very high loads and under conditions of defective lubrication.

Lubricants for Moderate Speeds.—At speeds exceeding 10 feet per minute with about int lubrication and 100 feet per minute with more or less imperfect lubrication, a lubricant, in the case of a journal or shaft, forms a fairly thick film which wholly or almost wholly separates the rubbing surfaces. The conditions under which this film forms have been fully dealt with in the chapter on the 'Theory of Lubrication' (p. 48). It may be mentioned, however, that when the loads are moderate (200 lbs. per square inch, or even more when the lubrication is perfect) the friction and also the formation of the film are wholly due to the viscosity of the liquid. But with heavy loads the bearing

surfaces are brought into contact at a point on the 'off' side of the brass, and when this is the case a liquid possessing oiliness to a marked degree is required to prevent seizing.

In the case of plane surfaces, such as slide-blocks, viscosity is not quite so important a property from a lubrication point of view as oiliness, and unless the loads be small (70 lbs. per square inch or thereabouts), a good fixed oil or a mixed lubricant must be used.

In selecting a lubricant for journals running under ordinary conditions of speed, greater attention should be paid to viscosity than to any other property, provided always that the loads do not exceed 200 or 250 lbs. per square inch ; for, by making the bearing surfaces of suitable materials, little harm will be done by the contact of the rubbing surfaces during the short slow-speed intervals of running. The lubrication must, however, be as perfect as possible. Indeed, it is owing to the imperfect lubricating devices so largely in use that expensive fixed oils have to be used in place of the cheaper mineral ones. These fixed oils are apt to become acid and to gum ; but in reservoir bearings carrying heavy loads, and properly designed to give perfect lubrication, the objectionable qualities of the fixed oils which it may be necessary to use are masked by a liberal admixture of mineral oil. Indeed, this form of bearing reduces the friction to the smallest possible figure, enables a cheap oil to be used, and economizes the lubricant.

For bearings carrying small loads pure mineral oils answer admirably, the viscosity selected being the smallest that will enable the oil-film to form properly. On the whole, the lower the speed the greater should be the viscosity, and the higher the speed the smaller the viscosity. This applies with special force to mineral oils. With increasing loads, especially if the lubrication be imperfect, it will be found that considerable wear and overheating will result unless fixed oils be added ; but it is only in exceptional cases, such as when the lubrication devices are poor, that pure fixed oils need be used alone. For locomotive engine work, about 25 per cent. rape oil and 75 per cent. mineral oil will generally work well.

Except in special cases, greases should not be used unless mixed with a good mineral oil, the oiliness of which they increase.

The bearings of railway vehicles are somewhat exceptional. They have to carry loads of as much as 380 lbs. per square inch, and often run at journal speeds of 9700 feet per minute, as well as very slowly. On this account, great care has to be taken in their lubrication and design. The bearings are made of white-metal or bronze, are long and narrow, are well lubricated by a pad placed beneath the journal, and are kept cool to some extent by the rapidity with which they pass through the air. With phosphor-bronze bearings, a mixture of 33 per cent. of mineral oil with 67 per cent. of olive oil is used by one large railway company noted for its freedom from hot axles.

Lubricants for High Speeds.—Quick-running spindles, dynamo shafts, and, indeed, all kinds of high-speed bearings, require ample

bearing areas and thin oils for their lubrication. The loads carried per square inch are consequently low, and pure mineral oils may be used with advantage. There are instances, however, where good lubrication is impossible, and to minimize the wear a good fixed oil must be used. The bearings for such speeds should always be so constructed as to keep the surfaces well supplied with oil without wasting it. When this is done, mineral oil containing about 10 per cent. of fixed oil answers admirably, for there is then little wear, and the frictional resistance is small.

Lubrication of Miscellaneous Machines.—The spindles of small machines, such as *clocks, watches, and other delicate mechanisms*, are generally made of hard steel. They work either in agate or other polished mineral bushes, or upon hard brass or bronze. The speeds are generally very slow, and the lubrication 'imperfect.' The pressures are also small, generally only a few pounds or ounces per square inch. The smaller spindles are carefully moistened with a fatty lubricant and put into position. The spindles then have the capillary spaces between them and their bearing surfaces filled with oil, which must often last for many months without renewal. The essential properties of a lubricant for such purposes are that it must be as free as possible from tendency either to gum or thicken by oxidation, or to corrode metal, and it must withstand exposure to temperatures as low as possible without becoming frozen or unduly thickened. The lubricants mostly used are porpoise and dolphin jaw oils, ben oil, hazel-nut oil, neatsfoot oil, sperm oil, and olive oil. The oil should be exposed for some time to a temperature rather lower than that to which the mechanism is likely to be subjected in use, and that portion of the oil which remains liquid should be separated by filtration and preserved for use. Any free acid should be removed by the process described on p 218. A little good mineral lubricating oil may with advantage be mixed with the fatty oil. Whatever oil be used, it should be proved by analysis to be genuine and free from excess of acid. The lubrication of clocks, watches, and such small machines requires great skill and experience, and, unless there be no alternative, it should not be attempted by any but an expert. Oil should be applied sparingly. If too much be used, it is drawn over the plate and the pivot is left dry.

For the *ring spindles of textile machinery*, which run in a bath of oil at speeds as high as 10,000 or more revolutions per minute, mineral lubricating oils of low viscosity, not exceeding that of sperm oil at 60° F., are used, generally pure. *Mule and throstle spindles* require an oil of higher viscosity, say from two to three times that of sperm oil at 60° F. Pure mineral oil is frequently used, but a mixture containing from 10 to 20 per cent. of refined neutral fixed oil is preferable, and is used in many cases. For *looms* a mineral oil of still higher viscosity, about 1·5 times that of olive oil, is used. In cotton spinning, some manufacturers still use sperm oil, either alone, or mixed with a limited proportion of mineral oil in order to reduce

the tendency to gum. In woollen spinning, mineral oil of about the same viscosity as olive oil at 60° F. is used, also olive oil itself, according to the class of work. As all pure mineral oils cause objectionable stains on cotton or woollen goods, which can with difficulty be wholly removed, it is customary to use either pure fixed oils, or mineral oils containing a large percentage of fixed oil, in all cases where the lubricant is liable to be splashed upon the fabric (see p. 463). For this reason, neatsfoot or lard oil is used for the lubrication of *lace-making machines*, but for some of the light bearings of lace-making and silk-weaving machines where oil is objectionable, graphite is used.

For *light sewing machines, and other kinds of delicate machinery running at high speeds*, mineral lubricating oil is used having about the same viscosity as, or even less than, that of sperm oil, preferably mixed with from 10 to 20 per cent. or more of sperm oil.

For *heavy sewing machines, printing machines, machine tools and other general machinery, shafting, etc.*, a mixture of mineral oil with from 10 to 20 per cent. of neutral animal or vegetable oil is suitable, the viscosity of the mineral oil employed depending upon the class of machine. The heavier the machine and the slower the speed, the greater the viscosity needed. Animal oils as a class are preferable to vegetable oils in such mixtures, because they are less liable to gum; and for the same reason the larger the proportion of mineral oil which can be used the better, provided the bearings are efficiently lubricated and run cool. Among the vegetable oils, neutral coco-nut oleine is one of the least oxidizable. Sometimes other considerations, such as fluidity at low temperatures, or cheapness, are of paramount importance, and lead to the employment of vegetable oils like rape, which are somewhat readily oxidizable.

Dynamos and motors with bath or ring lubrication are lubricated with mineral oil having from two-thirds to about three times the viscosity of rape oil at 60° F., according to the power, weight, and speed of the machine. The mineral oil is preferably used pure.

For turbine bearings (forced or circulating pump lubrication) pure mineral oil is used having a viscosity ranging from one to five times that of refined rape oil at 60° F., according to the weight and speed of the turbine and the temperature at which it has to work.

For the *forced lubrication of high-speed engines*, pure mineral oil of about twice the viscosity of rape oil at 60° F. is suitable. It is important that the oil used should separate readily from water, and be easily filtered whilst in circulation.

For the *splash lubrication of high-speed steam engines (Willans type)*, charcoal filtered mineral cylinder oil of medium viscosity mixed with a very little (2 to 5 per cent.) of lard oil answers well. The same oil should be used for the cylinders of the engines. The proportion of oil to water in the bath should be about one to ten. Soft water should be used.

For *locomotive and tender axles and machinery* mineral oil having

from two to four times the viscosity of rape oil at 60° F., mixed with
refined rape oil in the proportions of three of mineral to one of rape,
answers well. For very heavy locomotives, especially in warm
weather, it is desirable to increase the viscosity of the mixture by
the addition of some good mineral cylinder oil, but dark natural
or reduced oils must not be used for this purpose, as they interfere
with the free siphoning of the oil through the worsted trimming.
In hot climates castor oil is used.

For *marine engine motion*, and *machinery working in hot places*,
mineral oil is used in admixture with blown or thickened vegetable
(usually rape) oil, the latter oil forming from 20 to 33 per cent. of
the mixture.

For the *lubrication of steam engine cylinders* heavy mineral
cylinder oils should be used, mixed with from 5 to 25 per cent.
of rape or other fixed oil, according to circumstances, always
endeavouring to reduce the proportion of fixed oil to the lowest
proportion necessary to ensure efficient lubrication. In some cases,
pure mineral oil must be used, or no oil at all, as in the cylinders
of marine and other engines working with surface condensers the
water from which is returned to the boilers. In such cases it
would be dangerous to use fixed oil, unless the condensed water
were completely purified from oil before being returned to the boiler.
Lubrication is improved by mixing a small quantity of graphite with
the cylinder oil, but unless the mixture be kept continually stirred
the graphite settles out and causes trouble. Chapman's automatic
cylinder lubricator, described on p. 453, has been specially designed
to feed such mixtures. Chapman & Knowles have also patented a
mixture of graphite and glycerin for the lubrication of steam engine
cylinders. The graphite is impregnated, before mixing it with the
glycerin, with a sufficient quantity of petroleum or other hydro-
carbon insoluble in glycerin to reduce the specific gravity of the
mixture to that of the glycerin, thus causing it to remain in suspen-
sion. Special advantages are claimed for this 'oil-less' lubricant in
cases where the condensed water of steam engines is used for feeding
boilers. For further remarks on steam cylinder and valve lubrica-
tion see p. 482.

For *gas engine cylinders* an oil very largely used is a mixture
containing, approximately, 90 per cent. of mineral oil and 10 per
cent. of neutral fixed oil, the viscosity of the mixture being about
the same as that of rape oil at 60° F. In the working of these engines
carbonaceous deposits are liable to be formed by partial combustion
of the lubricant, especially when used in excess, which not only foul
the cylinders and passages, but, with high compressions, frequently
cause troublesome pre-ignition of the explosive gases. For this
reason, the mineral oils selected for lubrication should be such as
have undergone very careful rectification and show the least tendency
to decompose and deposit carbon when heated. They should also be
oils of low volatility, *i.e.* not losing appreciably by evaporation at

working temperatures; and it would certainly appear desirable to exclude as far as possible any admixture of fixed oils, seeing that these are not capable, as are the mineral oils, of being volatilized without decomposition. The use of pure mineral oil of suitable viscosity and low volatility has been found to give excellent results in the author's experience with gas engines, as well as being cleaner in use and cheaper than mixed oils. Veitch Wilson, however, informs us, as the result of extensive practical experience, that many *oil engines* can only be run with either pure fixed oils such as olive, lard, or neatsfoot, or with mixtures largely composed of such oils

The deposits which are found in gas and oil engine cylinders are not always wholly formed from the lubricant. A deposit of carbon may sometimes be due to incomplete combustion of the gas or oil vapour, if the air supply is deficient: sulphur and compounds of sulphur not infrequently met with are derived from the fuel. We give analyses of three deposits, two taken from the pistons of gas engines, and one from a gas-valve chamber, which have come under our notice. The first was from an engine lubricated with a dark Russian mineral oil, and is a typical gas-engine cylinder deposit.

Non-oily organic matter (chiefly carbon),	59·8
Oily and resinous matter,	26·3
Sulphur (free),	·4
Ferric and ferrous sulphates (soluble in water),	1·1
Ash (chiefly ferric oxide),	11·1
Water,	1·6
	100·0

The second was from an engine lubricated with a pale American mineral oil. The ammonium sulphate was due to imperfect washing of the gas.

Non-oily organic matter,	58·4
Oily and resinous matter,	17·1
Sulphur (free)	·8
Ammonium sulphate, etc., soluble in water,	12·7
Ash (chiefly iron oxide),	8·5
Water,	2·5
	100·0

The third, found in the gas-valve chamber of a gas engine, was remarkable in containing 50 per cent. of free sulphur, clearly derived from the fuel. It contained :—

Free sulphur,	50·0
Oil soluble in ether,	17·0
Combined fatty acids, air, etc.,	13·0
Ash (chiefly iron and copper oxides),	15·0
Water,	5·0
	100·0

The lubrication of *motor cars* is a special case of the lubrication of high-speed gas and oil engines and machinery. For the chamber lubrication of the engines, mineral oils of high viscosity must be used, on account of the high working temperatures, and they must be selected for petrol engines on the same principles as for gas and oil engines, *i.e.* carefully rectified oils from good crude petroleum must be used, not readily decomposed by heat, and not losing appreciably by evaporation at working temperatures. Whether the mineral oil be used alone or mixed with fixed oil, and what proportion of fixed oil should be added, must depend upon the conditions which obtain in the particular engine. For the machinery of motors lubricated on the circulating pump system, where the oil is drained from the bearings into a reservoir, filtered and re-used, the lubricating oil should be pure mineral of no greater viscosity than is needed to keep the bearings cool; any viscosity in excess of this involves increased friction and waste of driving power. Motors lubricated on the drop sight feed system should be supplied with a mixture of mineral and fixed oil. For certain bearings, grease cups are used, and for these care should be taken to select greases which melt at a suitable temperature and do not separate, *i.e.* the oil in the grease must not run down and leave the soap in the cup, but the grease must melt as a whole.

For the cylinders of *steam motors* fitted with flash boilers like the 'Serpollet,' the 'Miesse,' or the 'Clarkson,' charcoal-filtered mineral cylinder oils are preferred. For those fitted with multi-tubular boilers, like the 'Locomobile,' 'White,' or 'Duryea,' natural mineral oils of high flashing-point are used.

For *steam lorries, traction engines*, etc., which work at high pressures, exhaust direct to the atmosphere and, as one maker says, 'cough' the cylinder oil out with every stroke, heavy dark oils are good enough, used pure for superheated and mixed with rape oil for saturated steam. For the splash lubrication of the engines of all steam motors and lorries pure mineral oils must be used, to avoid emulsification with water.

The *ball-bearings and chain pins of cycles and motor vehicles* work under heavy pressures and comparatively slow rubbing speeds, for the slip of the contact faces of the balls upon their bearing surfaces is very small. The conditions under which slip takes place in such cases, and the real part a lubricant plays, can only be explained by the theory of Osborne Reynolds (see Chapter I., page 12). Here we are concerned rather with wear than friction, and such friction as exists is low speed. On this account a good neutral animal oil or fat, pure or mixed with a fairly viscous mineral lubricating oil, is the most suitable. The chain of a cycle or motor, both as regards the friction of the pins and of the links on the teeth of the wheel, works under conditions which require a good grease or a good fatty oil. Sperm oil mixed with a little vaseline to thicken it, and with plumbago to keep the surfaces from grinding if they should

become a little dry, answers well for cycle chains. Rangoon jelly mixed with graphite (Price's 'Rangraphine') also gives good results and lasts well. Excellent results are also obtained if running the chain through a bath of pure sperm oil, or a mixture of good mineral oil with a little refined animal oil, which is held in a suitable case secured to the machine. Pure mineral oils seem quite unsuitable, as with them the bearing surfaces are apt to wear unduly. Except where an oil-bath is used, a thick oil or grease is necessary for the chain, as a thin liquid rapidly runs off. If properly protected from dust and dirt, and suitably lubricated, a cycle chain ought not to require tightening up more than once or twice in a year. For motor chains, a neutral animal fat or good neutral grease (soap-thickened oil) mixed with graphite is recommended, such as Price's 'Cirogene,' which is a lubricant of this nature further stiffened by the addition of wax.

For *very heavy bearings*, solid substances, such as soapstone, graphite, asbestos, etc., are sometimes used as lubricants. They cannot easily be squeezed or scraped from between rubbing surfaces, and are, consequently, suitable where very great weights have to be carried on small areas, and where the speed of rubbing is not high. Indeed, some solid lubricants will sustain, without injury to the surfaces, pressures under which no liquid ones would work. As a rule, the bearing surfaces are made of exceedingly hard materials. Between cast-iron surfaces plumbago has been found to give good results. T. Shaw found it to be superior to oil for the tables of heavy planing machines.

For the *hot-necks* of rolls, pitches of various kinds are used, alone, or mixed with heavy mineral lubricating oils, or the latter may be thickened with soap, etc.; see p. 131.

Hydraulic Machinery.—In hydraulic machinery many of the rubbing surfaces of the spindles, valves, etc., are in a great measure bathed in water, and such lubricants as can be used for them must be carried by the water. When the same water is used over and over again, mixed with as much fresh water as is necessary to meet the waste due to leakage through glands, etc., it is treated in the tank from which it is pumped and into which it is returned from the machines. In such case, soft soap alone appears to be the best lubricant, but a little mineral or fatty oil may be added. The soaps formed in or added to the water concentrate upon all the surfaces with which the fluid comes into contact, and form very tenacious films which prevent the cutting and grinding of the valve faces.

When the water is obtained from street mains, and is passed after use into the drains, the lubricant is generally added drop by drop by means of a lubricator actuated mechanically by the hydraulic machine. The rate of supply is thus regulated in accordance with the volume of water passing. When the pressure is below 750 or 800 lbs. per square inch, a mixed mineral and animal oil answers well, but for higher pressures soft soap is a better lubricant. Hydraulic rams,

slides, guides, etc., in cool climates may be lubricated with tallow, provided it be free from acidity, as this lubricant does not alter much at ordinary temperatures.

Nuts, keys, etc.—To enable nuts, boiler wash-out plugs, keys, etc., to be easily placed in position, and removed again after standing, it may be for months or years, in warm places, a lubricant is required which keeps its nature and does not evaporate, corrode, or otherwise injure the metallic surfaces. For such purposes, tallow, or other fat or oil, or greases containing them, should on no account be used. No doubt they make the nuts, etc., work freely in the first instance, but in a very short time the fat undergoes a change which effectually corrodes the surfaces together. Even a mineral oil, although it does not set up corrosion, flows out of the joint in the course of a few hours when heated, evaporates, and leaves the surfaces free to 'bind.' To prevent this, the best plan is to make use of a lubricant consisting of a thick mineral cylinder oil or petroleum jelly mixed with black-lead. Here, even if the fluid or semi-solid portion of the lubricant should be driven out of the joint by capillary forces, the black lead remains in the joint, keeps the nuts, etc., free, and enables them to be easily tightened or taken off at any time without risk of breakage or damage.

However, there are cases where no lubricant must be used, such, *e.g.*, as the nuts of the bolts securing fish plates to rails, which, if lubricated, would be apt to slacken back. The same may be said of the bolts securing many of the parts of machines subject to vibration.

Boiler Fittings.—The valve spindles, valves, etc., of fittings attached to steam boilers are apt to work rather stiffly owing to the difficulty of lubricating them, and the rapidity with which most lubricants leave the heated surfaces. For them the mixture described above for nuts, etc., answers well, the lubricant in all cases being a mineral cylinder oil or grease containing a lubricating solid such as black-lead or French chalk.

The glands of low-pressure boiler fittings may be packed with hemp or jute soaked in paraffin wax containing French chalk or black-lead. *The soft solid lubricant should on no account be a fatty oil or grease.* Such lubricants attack the metallic surfaces with which they come into contact and cause the glands to leak. For high pressures, or in very hot positions, the hemp must be replaced by asbestos cord or metallic packings.

Some enginemen have adopted the practice of putting oil, or the waste water from their cylinder lubricators into steam boilers, either through the injectors or into the feed water. This practice is one which should *not* be adopted under any circumstances, for the acids thus passed into the boilers or formed there by decomposition of the fixed oil which most cylinder lubricants contain, give rise to or seriously accelerate the rate of corrosion which often results from the strains set up in the metals by changes of temperature, etc.

Lubrication effected in this way not only endangers the lives of those who adopt the plan, but is sure to seriously shorten the life of the boiler, especially if the water be soft. If the water be hard, greasy deposits are formed, which are apt to cause overheating and collapse of flues, etc.

Cutting Tools.—The cutting edge of a tool, such as that used for a lathe, drill, slotting or other machine, is, owing to its hardness, enabled to embed itself in the softer metal. When the metal is being worked, especially if it be a tough one, heat is developed, not only owing to the friction against the tool, but also owing to the distortion suffered by the strip cut off. A large proportion of the heat developed distributes itself in the mass of metal, while some of it spreads to the tool, raising its temperature and occasionally seriously injuring its temper. To prevent this, a stream of liquid is directed against the tool. Water is generally used, but owing to the rapidity with which plain water rusts clean iron surfaces, it has to be mixed with soap of some kind, which also acts as a lubricant.

At the cutting point there is actual metallic contact, and the friction is mainly that of an unlubricated surface, *i.e.* the friction decreases with increasing speeds of cutting. The increase of speed consequently decreases the load on a drill, although the heat produced may be somewhat greater. On this account it is well, should a drill break, to first try a higher rather than a lower speed, unless the heating effect produced be already too high to admit of such a change.

In many shops the speeds of machines are lower than they need be, for it is sometimes assumed that breakages can only be prevented by running at low speeds. Mineral oils, being deficient in oiliness, are not suitable for high-speed tools which require good lubrication. Fatty oils such as lard oil, or a mixture of soft soap and soda, from 14 to 16 lbs. of such to 100 gallons of water, are greatly superior. The water, having a high specific heat, keeps the tools cool, whilst the soap and soda improve its lubricating qualities as well as prevent the surfaces from rusting (see p. 131).

The exact effects produced by a lubricant upon the working of a cutting tool, at least so far as driving power is concerned, are not clear, as pointed out. That the lubricant penetrates to the neighbourhood of the cutting edge is shown by the increased smoothness of the finished surface, and by the greater force required to keep the tool against the work. The lubricant finds its way almost, if not quite, to the cutting edge through the gap at A (fig. 154). The edge of the tool, being

Fig. 154.

lubricated best on the side A nearest the work, is unable to dig in and tear the metal, which is, therefore, finished smooth and partially burnished. All bearings should be finished with a very sharp and well-lubricated tool no emery being used if the metal be at all soft.

Steam Cylinder and Valve Lubrication—*Imperfect Nature of.*—
Although it is possible to so lubricate the cylinders and valves of
a steam engine that there shall be no excessive wear, it is impossible
to obtain anything like the results, so far as friction is concerned,
given by a well-lubricated journal. The pistons and valves move to
and fro in straight lines, and do not tend to automatically place
themselves in such positions as to trap the oil properly and keep the
surfaces from touching. Neither can the large extent of surface
exposed be kept flooded with oil, the passage of live steam through
the valve-chest and cylinders not admitting the presence of large
quantities of oil. We have, therefore, to be content with the presence
of a lubricating film of no great thickness, and either make the loads
on the bearing surfaces small or cause them to move somewhat
slowly.

For a proper understanding of the conditions under which the
efficient lubrication of steam-valves and cylinders takes place, it is
necessary to consider at some length the physical properties both of
the lubricant and of the steam.

Evaporation of Oil.—Even at ordinary temperatures water, when
in a dry atmosphere, evaporates, the vapour mixing with the air
and making it moist. Such evaporation goes on until the air is
saturated with moisture. Somewhat similar conditions occur at
the free surface of a mineral oil. Such oils slowly evaporate until
their vapours saturate the air or steam in contact with them.
With ordinary bearings at ordinary temperatures there is very little
loss by evaporation, when oil of good quality is used, but at the
high temperatures of steam cylinders serious loss may occur, for
not only is the tendency to evaporate increased, but the oil vapour
is rapidly carried off with the great volume of steam passing
through the exhaust. On this account, mineral cylinder oils should
be carefully tested as directed on p. 191, and all that are unduly
volatile rejected.

Decomposition of Lubricants.—Vegetable and animal oils are unsuit-
able for cylinder lubrication, as, in contact with steam, at the high
temperatures to which they are subjected, they undergo a chemical
change resulting in the formation of free fatty acids (p. 105) which
may give rise to very serious corrosion. In many instances, the use
of such fatty lubricants has resulted in the cylinder metal being
rendered quite spongy and porous in the course of a few years: bolts,
valve-spindles, studs, and other parts have been cut quite through,
and cylinder joints, etc., rendered leaky.

The steam passages also become choked with metallic soaps,
oxides of iron, and free carbon, resulting from the chemical action of
the fatty acids upon the cylinder metal and the destructive decom-
position effected by heat and high-pressure steam. In locomotives
the oil thrown against the hot blast-pipe, and even that adhering to
the ports undergoes destructive distillation with formation of a
carbonaceous deposit, which accumulates and gradually blocks up the

passages. A partial analysis of such a deposit scraped from a piston head is given below.

Fixed carbon	35·37
Hydrocarbon soluble in ether,	7·52
Neutral fatty oil,	3·07
Fatty acids, free, and combined with metallic oxides,	2·52
Ash; chiefly, oxides of iron, with small quantities of copper oxide, lead oxide, etc.,	44·85
Moisture,	2·21
Undetermined and loss,	4·46
	100·00

Fatty oils, however, when mixed with mineral oils, in quantities not exceeding 5 to 20 per cent., do not seem to produce these objectionable results so readily ; indeed, the lubrication of parts which have to carry very heavy loads is greatly improved by the addition of such oils.

When surface condensers are used, and the condensed water is again passed into the boilers, great care must be exercised to prevent the passage of the oil used for the lubrication of the cylinders into them. Tallow, suet, castor oil, and other animal and vegetable lubricants must not be used in such cases, even in small quantities, for the acids liberated by the action of heat and water vapour pass into the boilers and cause serious corrosion. These acids cannot be separated from the water by merely allowing it to rest for a time in a tank ; they remain to a large extent suspended in the water, giving it an opalescent appearance. Mineral oil also remains suspended in condensed water in a very fine state of division, and even though a considerable quantity may rise to the surface and be removed, sufficient may remain in suspension to produce very serious effects upon the flues. Indeed, its presence may so check the passage of heat through the boiler plates as to cause them to collapse. When the water is passed through an efficient filter before entering the boiler, and is thereby made bright and clear, no corrosive action appears to take place, the grease, etc., being for all practical purposes eliminated.

The deleterious effects produced by the action of a lubricant on marine boilers, when surface condensers have to be used, have led to marine engines being run without any direct lubrication whatever of their steam-chests or cylinders, though a certain amount of oil finds its way in from the swabbing of piston rods, etc. This can often be done without any very serious wear taking place, for the load on the rubbing surfaces of many well-designed engines is very small, but with new engines slow speeds must be adopted to begin with, and the surfaces allowed to 'burnish' and acquire hard skins. For remarks on the use of graphite in cylinder oils, and of mixtures of glycerine and graphite, see p. 476.

Application of Cylinder and Valve Lubricants.— Even when the lubricant used for cylinders is a good one, it is sometimes found that

the parts are imperfectly lubricated. This may arise from several causes, most of which, however, can be traced to superficial tension phenomena.

It has already been explained that water will not touch the oiled surface of a solid, although the relative superficial tensions of metal, oil, and water are such that the latter has a greater affinity for the metal than oil has. But oil cannot be readily moved from a metallic surface by water, for the oil is nearly insoluble, and evaporates very slowly. On the other hand, water may be readily replaced by oil, owing to the facility with which the water evaporates and leaves a comparatively clean surface for the oil to cover. The superior affinity of a metallic surface for water rather than oil is also shown by the rapidity with which water will displace the oil from a bearing where there is abrasion going on, and will cause it to run hot. The presence of water in a steam-cylinder or steam-chest is consequently deleterious. The friction of the faces rubs off the oil, and if water be present in bulk, it covers the surfaces, and if the loads be heavy, they grind and tear in the absence of a lubricant.

The condensation which takes place in a long steam-pipe will often send so much water into the engine cylinders that lubrication becomes impossible. To prevent this, separators are fitted so as to dry the steam before it is used. A vertical exhaust pipe not fitted with a drain pipe to carry away the water will also cause wear and tear of the valves, for the water condensed in the cylinders cannot get away freely. Difficulty is often experienced when valves are placed on the top of the cylinders, for the water in the cylinders and steam-chest cannot escape, but remains on the cylinder bottom and the valve faces.

The D valves of non-compound high-pressure engines, especially when not balanced, press very heavily upon their faces, but the stroke being small, and the speed of rubbing low the heating effect is not large. The pressure upon them, however, is so great, that where at their ends there is any considerable length of valve seating which, owing to the short stroke, is not exposed to the steam, the surfaces are apt to grind and tear.
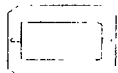
FIG. 155.

To ensure the proper lubrication of this part of the valve face, grooves may be cut in it, as shown in fig. 155.

We have in a previous chapter described one or two forms of lubricator designed to steadily introduce a lubricant into the steam spaces without entailing loss of either steam or oil. Such a lubricator is generally placed above the point where the steam-pipe enters the steam chest. It must not be placed above the main steam-valve, for when the engine is not at work, the steam-pipe may become filled with condensed water and the lubricator allowed to feed into it. Rising up the water-logged steam-pipe, the oil will flow into the boiler, and may cause serious injury there. The pipe conveying the oil from the lubricator should be carried well into the

steam-pipe, so that the lubricant may be delivered into the rapid current of steam and not allowed to run down the sides of the pipe. Indeed it is a good plan to carry the oil-supply pipe right across the steam-pipe. and allow the oil to escape through a number of side perforations. When this is done, the oil escapes at several points, is well distributed over the column of steam in the steam-pipe, covers the surface of each particle of water passing with the steam, or is carried as spray to all parts of the steam-chest. The water particles, being covered with a pellicle of oil, then lubricate instead of merely wetting with water the surfaces upon which they impinge.

Management of Machinery.—*Cleanliness.*—One of the first points to be attended to, if machinery is to be kept in good order and work satisfactorily, is cleanliness. We have already pointed out the necessity of keeping grit and dirt of various kinds out of the lubricants used. But rapid wear and even overheating may result from dust blown about the engine or machine room. On this account, proper care should be taken to prevent the accumulation of dust in corners, louvres, etc., for in windy weather it is liable to be suddenly scattered over the machinery. And en, every precaution should be taken to prevent the admission of grit and dirt, the floors being moistened and swept repeatedly, and every corner scraped clean. In many cases it is well to cover motors, dynamos, etc., when not at work, by canvas coverings.

The extent to which proper care is taken to keep the machinery in order and in proper running condition, is nearly always reflected by the general appearance of the installation. Carelessness of management go hand in hand with dirty machinery and untidy engine-houses and shops. In many of our modern engine-rooms, dust, dirt, and scattered oil or waste are considered as much out of place as they would be in a dwelling-house.

The nature of the task imposed upon the engineer in charge of an engine-room or mill depends largely upon the design of the machinery he has to look after. As extreme cases we may contrast the huge, slow moving pumping engine of the last decade with the comparatively light, high-speed motors furnishing power for a modern electric-light station. In the one case lubrication is generally effected by the cheap, imperfect siphon arrangements, and in the other by the more modern automatic methods giving perfect lubrication. On the score of satisfactory running there is little to choose between the two methods, but the older machines cannot compare as regards first cost and economy with the more modern designs. But it frequently happens that steam, gas, and oil motors are made to run at speeds for which their lubricating arrangements are quite unfitted, and it is only by the exercise of the greatest care that casualties can be avoided. Free lubrication and good fatty oils being necessary, splashers have to be fixed in such a way as to prevent the oil from being thrown about, and tins placed to catch that portion of the lubricant which is ejected at the ends of the brasses.

High speeds may be considered as ranging from 500 to 15,000 revolutions per minute, the higher speeds being generally confined to comparatively small spindles transmitting considerable power, and the lower speeds to shafts several inches in diameter. To run successfully, the lubrication must always be good, for the least failure in the oil supply causes the bearings to run hot. To ensure successful running, the oil-bath principle should be adopted, the lubricant being thrown continuously *over* the portion of the bearing on the opposite side to that of the brass which carries the load. This may be effected either by the action of a disc, chain, or hoop on the shaft, or by a small pump raising the oil from a reservoir below the bearing.

In some high-speed bearings for shafting, which have only an imperfect automatic supply, additional cups filled with grease are placed at the ends of the bearings. Should they run hot, this grease melts, runs out, lubricates the rubbing surfaces, and prevents for the moment any serious injury. The covers of such grease cups often rest upon the grease and fall, when it runs away, thus warning the man in charge of the need of re-lenishing.

At the present time the whole tendency of modern engineering is to run every machine at its greatest possible speed, and thus get a maximum amount of work out of a motor of minimum size and weight. To enable this to be successfully accomplished, the new methods of lubrication have to be adopted and the old loose methods of engine-room management replaced by methods which entail constant watchfulness concerning the details of lubrication.

The attendant in charge of high-speed machinery must exercise all possible care and attention, for, as we have pointed out, machines are frequently made to run at speeds for which the methods of lubrication adopted quite unfit them.

Starting of New Machinery.—To ensure the proper working of any such complicated piece of mechanism as a steam engine, especially if it be run at a high speed and with a heavy load on the bearings, or if the work transmitted or developed be large, much depends upon the intelligence of the erecting fitter or of the engineman who sets the machine in motion. Of course the bearings may be so designed that, owing either to the strains set up by the stresses acting on them, or to the expansion of the parts from the heating of the cylinders, etc., the rubbing surfaces are pressed together with undue force in places, and cannot possibly run cool without some small alteration being made or additional clearance given. Upon the engineer in charge, therefore, falls the duty of making good such defects in the bearings, or their method of lubrication, giving freedom to certain parts, such as slide bars, to expand so that they may not buckle with changes of temperature, putting in lubricating grooves, etc., where they have been omitted, arranging for the proper escape of condensed water from the cylinders, and taking care that all the surfaces have been properly bedded together. All omissions detected or alterations

made should, of course, be carried out with the cogizance of those responsible.

Even when all precautions have been taken, a machine will seldom run cool if it be at once worked with the full load on or at its maximum speed. This arises from the fact that for good lubrication, and to obtain a low coefficient of friction, the working parts must bed themselves together in a way which a fitter is quite unable to imitate. Indeed, in a short time all bearings, if properly designed, are worn to a shape which enables the lubricant to be drawn in between the surfaces and wedge them apart. When this shape has once been attained, further wear at running speeds almost ceases, especially if suitable methods of lubrication and proper lubricants be used. The machine should consequently in the first instance be run with a light load at a very low speed. Under those conditions the wear is comparatively rapid, especially if a moderately thin mineral oil be used and the journals and pins be allowed to bed themselves in the brasses. The speed should then be increased, and the blended oil used when, after some hours' running, the working speed has been attained. During this stage it is well to supply the lubricant liberally, to prevent overheating.

In the case of railway vehicles, even when the greatest care is taken, a journal may run hot; it then becomes necessary to change the brass. A hard white-metal or bronze bearing cannot be expected to run well at first, even if very carefully fitted, for, as stated above, the correct form of the surface can only be brought about by wear, and whilst such wear is going on at high speed the heat developed may be very great. To enable a vehicle, a bearing of which has become so hot as to damage the rubbing surfaces, to be run at once, a new brass may be put in with a lead surface about $\frac{1}{16}$ inch thick. This rapidly beds itself upon the journal in such a way as to form a good surface where the journal is smooth, and does not bind heavily where the journal is damaged. A lead surface of this kind, H. R. Haigh states, will run several hundred thousand miles without being worn off.

Methodical Habits of Lubrication.—The most prolific source of trouble experienced with machinery arises from the occasional failure of the attendant to give each bearing its proper supply of oil. No doubt an unsuitable oil, the presence of grit, or some such cause may easily result in overheated bearings, but as a rule there must be a practically complete failure of the supply to give rise to a casualty. That this may happen very easily will be recognized when the number of bearings to be oiled in some machines is remembered; for a single oil-hole or cup missed during a round of oiling will often lead to grave results. Each bearing and rubbing face of a locomotive, for instance, must be lubricated before starting, each bearing receiving a sufficient supply to last for about 150 miles. In this case forgetfulness, or the non-adoption of a good system of oiling by the driver, may delay an express train for hours.

To minimize the trouble arising from such causes, the engine attend-

ant should systematically examine and occasionally feel the metal of all bearings, so as to detect any case of overheating in its early stages, and, when oiling a machine, should proceed in the same manner on every occasion, always taking the bearings in the same order, so as to reduce the risk of missing any. Even in the case of the sewing machine or cycle, this should be carried out. With such machines there is a descriptive pamphlet often given, showing each oil-hole numbered. By following the instructions and giving each hole, etc., oil in the order stated, it will be almost impossible for any important bearing to seize. In the case of a locomotive, the driver should commence at the leading end, say on the right-hand side, and then systematically oil each bearing as he moves towards the end of the tender and back along the left side of the engine to the front again. By adopting some such methodical plan, the risk of missing any bearing and thereby causing a failure is reduced to the smallest possible proportion. The same plan should be followed in putting the trimmings into the oil-holes of siphon lubricators before starting from a station.

Examinations of Bearings. - Assuming that all the bearings and lubricated surfaces are in good condition after a motor, machine tool, or mechanism for the transmission of power has been set to work, it by no means follows that they will continue to remain so for more than a few months without being properly cleaned and small defects made good. Careful periodical examinations must therefore be made of each bearing, for it frequently happens that valves wear out with unexpected rapidity, oil-ways become choked with metal or dirt, brasses fracture along the crown, white-metal partially runs out of the recesses prepared for it, lubricating pads become glazed, and a hundred other defects reveal themselves. In the case of a locomotive or a motor driving an electric-light station, any such failure will, if not discovered and remedied in time, lead to a breakdown, and either delay a train or temporarily extinguish the lights.

Although it is advisable to examine bearings at stated intervals, yet, unless they have been getting warm or knocking, or there is some defect or flaw which requires attention, the parts taken to pieces should be replaced exactly as they were when removed. It is a great mistake to always refit or reked the brasses, for it is impossible to give the surfaces the form which gives the least frictional resistance. Wear alone can do this. Examinations should, therefore, be confined to seeing that all the parts are sound, 'tinkering' with the rubbing surfaces being avoided as much as possible. Indeed, a well-designed and properly cared-for engine should run for years without the use of either a file or a chisel, provided it be kept clean and the lubricating appliances be always in good working order.

In dusty or dirty situations, where the oil has a tendency to thicken, or in cases where the wear of the bearing or shaft is considerable, deposits are apt to form in the oil-ways and prevent the proper flow of the lubricant. To prevent such deposits from collect-

ing to a serious extent, pedestal caps, etc., should be   asionally removed and clea ed.

When pad-lubrication is resorted to, it is necessa. y to remove the pads every few weeks and clean the surface which comes in contact with the moving surface, for the wool often becomes glazed by the metallic surface against which it rubs. The pad must, therefore, be scraped clean and well oiled each time it is removed, *i.e.* about once a week. Unless this be done regularly and often, the bearing will not keep cool and wear well.

Trimmings also require frequent examination and renewal. In warm places fatty oils gum and clog the pores, as does dirt in dusty places. Want of proper attention to trimmings is a fruitful source of heated bearings, for the volume of oil supplied by them varies with the number of strands or with the fit of the woollen plug in the oil-hole. Any change either in the fluidity of the oil or in the cleanliness of the pores also alters the rate of supply to the bearing.

Where the lubricant is supplied by oil-cups fitted with small valves at the bottom in such a way that the rate of feed may be judged by the rate at which the oil falls from a small nozzle, the passages are apt to become suddenly clogged by mucilage or dirt stirred up from the bottom of the reservoir. They should, therefore, be regularly examined and cleaned out. The oil should also be removed periodically from all reservoir bearings, filtered, and, if not too acid, used over again.

Examination Book.—To ensure the examinations being really made at the required intervals by those whose duty it is to attend to such matters, an examination book should be kept in which is clearly stated the nature of all periodical examinations, a column being provided for the engineman or fitter to sign after having made each inspection.

The necessity for adopting this course is the greater the larger the station or mill, and the more numerous the machines of various kinds it contains. Such machines, motors, or lines of shafting must be cor ec ively numbered, so that they may be easily identified and the entries referring to repairs or examinations properly kept up.

If such a book be not kept, the engineer in charge cannot expect each motor, &c., to be properly and regularly attended to, for some portions of the machinery will receive undue attention, whilst others will be neglected, and all sorts of difficulties will arise which a better organized system would prevent.

Preservation of Machinery not in Regular Use.—It frequently happens that an engine plant for the supply of power is put down in duplicate, and parts may have to stand idle for weeks or even months. Whenever possible such engines, etc., should be worked alternately, so that all the surfaces may be kept clean, smooth, and in good condition. When such motors as marine engines have to stand idle in dock, it is well to get up steam occasionally and run the engine for a few hours. Should this be impossible, the engine must be 'pinched'

round once each day to keep the cylinder faces in good order. Discs fitted with teeth are often keyed on to the shaft for this purpose.

Protection of Polished Surfaces. In cases where an engine or machine is to lie idle for any length of time a better plan is to *take the parts to pieces*, clean *all* the rubbing surfaces, and cover them with a protective paint. The same treatment should be accorded to accurately machined faces which are to be used for rubbing, and, indeed, all light work which is to be kept ready for use, as soon as it is finished. Unless this plan be adopted, the bearing surfaces will become pitted and rusted to such an extent that the machine will cost more to repair than it is worth.

The most commonly used mixture for this purpose is one consisting of white lead and tallow. It forms a good cover when put on warm, and it does not corrode the metals as the acid constituents of the tallow, if there be any, are converted into lead soaps. The white-lead in this mixture plays the part of the lime or soda in the numerous axle or other greases. Neutral petroleum jelly is also very effective in preserving bright steel from rust, if the surfaces to which it is applied are perfectly dry.

When the machinery is for export purposes, and may be exposed to rain or moist air, the surfaces must be covered with black enamel or green, which effectually protects them from rust, even if they should be immersed in water for many hours.

Overheating of Bearings.—We have already mentioned a number of causes which may lead to overheating, which should have been provided against either whilst the machine was being erected or during the preliminary or trial runs. It sometimes happens, however, that a bearing may run short of oil for a few minutes, or that grit may get between the surfaces and cause trouble. When this occurs to a marine engine bearing and the damage likely to be done to the engine is less serious than that which would result from the stoppage of the vessel, it is the custom to turn a stream of water, if possible soapy water, upon the heated parts and keep going. In many cases plumbago thrown over the heated surface, or run on to it mixed with oil, will prevent serious injury. Much the same may be said of a locomotive bearing as regards the advisability of stopping, but here nothing must be done which will endanger the safety of the train. Electric-light engines, where they are in duplicate, and most other motors, machine tools, etc., can be stopped for examination at once. Unless this be done promptly, the injury sustained may necessitate a new step or journal.[1]

In all cases of sudden heating it is wise to at once use a good fatty oil, as this kind of oil does not to the same extent as mineral oil, lose viscosity with rise of temperature, and the fixed oils are more 'oily.' A can of rape or olive oil may be kept handy for such emergencies.

To run without attention a bearing which becomes heated day after day is a great mistake, as there must be something radically

wrong to cause such heating. The shaft or journal may be oval, one or other of the surfaces damaged, grooved, or flawed. the oil-ways blocked up, the footstep distorted by overheating, the lubricator working improperly, the shaft sprung out of line, etc. It might not appear at first sight that a mere crack in the crown of a brass, especially as it scarcely affects the area of contact, would cause trouble. But it must be remembered that such a crack allows the oil to escape, and largely reduces the carrying power of the oil-film.

C. W. Naylor[1] mentions a case where two 5-inch diameter shafts, carried in plain babbited cast-iron bearing boxes split on a horizontal plane, each shaft transmitting power by belting from a steam engine to five electric generators, persistently ran hot when lubricated with oil or grease. As the pull of all the six belts on each shaft was horizontal, the oil was probably forced out through the split in the cores. However, it was eventually found possible to lubricate these bearings with water, a small stream being allowed to trickle through the bearings whilst running, and oil being fed into the bearings only during five minutes before closing down, in order to prevent rusting. The wear on the babbit and boxes during eleven years, whilst lubricated with water in this manner, was found to be only ¼-inch, and on the shaft nil. The temperature of the engine-room was about 100° F., the water varying in temperature from 45° in winter to 65° in summer. The shafting ran quite cool.

The real condition of a bearing which habitually heats can only be ascertained by taking the parts to pieces, and when this has been done there is no excuse for not making every defect good.

Bearings which fit too closely are very apt to run hot; on the other hand, those which are too loose make a great noise, and the repeated blows not only tend to produce and develop flaws in the moving parts, but also to damage the surfaces. What should be aimed at is a free bearing in which there is room for the oil-film to form.

Friction and serious heating may be produced by using a lubricant either too low or too high in viscosity. When the viscosity is too low, the oil-pressure-film, which keeps the bearings of rapidly moving machinery from touching, does not form properly, and solid friction results. On the other hand, when the viscosity is too great, the frictional resistance of the film may be so large that the bearing becomes warm or even hot. That it is best to use an oil having as small a viscosity as possible has been demonstrated over and over again especially when, as in the case of textile or printing machinery and dynamos, the bearings run at high speeds and the loads per square inch are small. The heat liberated, and therefore the friction encountered, is proportional to the internal friction of the lubricant, and when it is remembered that at high speeds there is a continuous film of oil separating the surfaces, and that the friction in journals and spindles is proportional to the viscosity of the oil, it is clear

[1] Trans. Amer. Soc. Mech. Eng., vol. xxvii. p. 432.

that heating is as likely to be due to the want of fluidity of the lubricant as to actual metallic contact action The best results are consequently obtained by using lubricants of the lo est permissible viscosity. Yet, frequently, the engineer in charge assumes that the heating results from the rubbing of the surfaces against each other, and is surprised to find that when he uses a thicker oil his bearings become still hotter.

Main engine bearings, the steps of which are separated into several portions, are very apt to run warm. This arises from the fact that to obtain good lubrication each of the brasses should be able to assume the relative positions, with regard to the journal, shown in fig. 102, p. 404.

When there is only one bearing step, the shaft or journal can place itself in the position necessary to give it carrying power, but, on the other hand, when there are two or three separate brasses, they must have freedom to move into such positions that there shall be a wider gap on the 'on' than on the 'off' side. The degree of freedom required is very small. The best way to secure it will depend in each case upon the adjusting arrangements.

It sometimes happens that a locomotive axle-box bearing, fed with oil through a hole and groove in the top of the brass, will run hot, and continue to do so, although every care has been taken to secure well-fitting faces. Now it has been repeatedly shown, especially with mineral oil, and, less markedly, with fatty oils, that when the oil is supplied in this way it is unable to properly wet the journal, being scraped off by the closely-fitting edges of the groove. Indeed, the better the fit of the brass and journal, the more the oil is confined , and prevented from getting to the proper place, viz., the 'on side of the brass. As a rule, the side play of the brass enables it to mount on the curves at the ends of the journal, and in this manner the oil is liberated and runs over the journal. A couple of small grooves from the oil-way to the ends of the brass will answer the same purpose and prevent overheating, provided the load be not too great (see also p. 400).

A siphon may cease to feed long before the oil reservoir is empty, and may thus mislead. The height to which the lubricant can be drawn from a reservoir by a trimming depends upon the fineness of the material of which it is made. Thus cotton wick will raise the liquid much higher than worsted. The latter material only lifts lubricating oil about 1¼ inches. Lubricator reservoirs are often made much deeper than this, and if not regularly cleaned out, they gradually become partially filled with a 'sticky, dirty mass. The better plan is to make them shallow and to clean them out often.

A bearing which habitually runs warm cannot be considered as working properly, even if it never actually heatses so badly as to necessitate a stoppage, for the coefficient of friction must be high and the waste of power considerable. Such a bearing has either got too much weight upon it, is not in line with other bearings on the same

shaft, or its surfaces are grooved and the oil-film cannot form. When this is the case, the shaft or journal, and also the brass, must be filed or machined to true faces. It occasionally happens that on taking the pedestal cap or brass from a bearing which has begun to get hot, the shaft or journal will be found to be badly flawed.

Selection of Lubricants.—Although it is clear that for each kind of bearing, speed, and load, only a comparatively few varieties of lubricants out of the great number placed by manufacturers on the market will be found to give equally good results, in practice the disadvantages resulting from having a large number of oils, etc., in use at the same time is so great that practical men, as a rule, prefer to use a few lubricants only, selected so that they shall answer as nearly as possible for all purposes. This limitation may, however, be carried to extreme lengths, and greater waste of power and damage to wearing surfaces caused than the convenience warrants

But the advantages to be gained by carefully selecting lubricants according to the kind of bearing to be lubricated are clearly becoming more and more marked as time goes by, for the speeds at which machines run are becoming greater and greater each year, as are also the loads placed on many of the bearings The conditions under which lubrication has to be effected are, therefore, rapidly becoming more diverse, and the time when the engineer could afford to use almost any lubricant placed on the market has passed away.

The scientific selection of lubricants can only be accomplished by ascertaining experimentally the extent to which different oils, etc., reduce wear and friction, for economy in the cost of oil is often only effected by greatly increased expense in other directions. This, the most important aspect of the problem of lubrication, will be dealt with presently.

Cost and Efficiency of Lubricants.—Although in the selection of lubricants the price is an important factor, there is no real economy in using cheap but unsuitable oils. This will readily be seen when the actual expense incurred in their purchase is compared with that spent on fuel and on repairs. Indeed, it has been maintained with some show of reason that the consumer can frequently better afford to use the highest priced and best article than a lower priced and inferior one supplied free of charge. This is certainly the case with small mechanisms, such as sewing-machines, clocks, and the like.

Not only may the loss by friction be largely increased by using an unnecessarily thick lubricant, or the bearings become clogged by using a gumming oil, but the wear and tear of the surfaces may become very great and the life of the parts be much shortened by using a lubricant deficient in *oiliness*. It is, therefore, imperative that the chemical and mechanical as well as the commercial, aspect of the question should receive careful attention, for many so-called *special oils*, for which a high price is demanded, are really composed of very cheap ingredients. The experimentally ascertained quality and not the price alone must therefore be the guiding principle in the selection of lubricants.

By means of the physical tests enumerated and described in detail in previous chapters, the viscosity, gumming properties, acidity, flash-point, etc., of various lubricants can be ascertained in the laboratory. If it were not for the fact that there is as yet some uncertainty regarding the methods of measuring the comparative oiliness of lubricants of different viscosities, there would be little difficulty in deciding which of a number of lubricants was the best to use for any particular purpose. Although mechanical testing machines, if properly used, give us some considerable information on this head, it is only by a knowledge of the extent to which each lubricant keeps the various bearings cool, and reduces friction and wear, that the engineer can judge properly whether he is obtaining the best possible result.

An accurate estimate of the comparative value of different lubricants can only be made by carefully ascertaining the frictional losses each lubricant entails and comparing these losses with the total work done by the prime movers. Knowing the cost of the fuel, etc., used, the engineer can then calculate how much he is expending in unproductive work with varying conditions of lubrication. By occasionally weighing his pedestal boxes, valves, etc., he can also measure the rate of wear going on in his machinery. A knowledge of such points will enable him at once to see whether he is losing or gaining by the adoption of any particular lubricant or lubricants, and also to note the effect produced by changes of temperature. Such knowledge is easily gained by fixing indicators on steam or other motors when all or certain parts of the machinery are running light, also when each machine has its full load, and again under normal conditions. In all cases when the power used is an important item, these observations should be made periodically, the results entered up for future reference, and a balance-sheet drawn up so as to enable the cost of power, and also of lost work, etc., to be compared with the expense incurred on lubricants.

Various **dynamometers** have been devised for measuring the power required to drive machinery. These instruments are introduced between the motive power and the machine, and measure the power transmitted, either by the compression of a spring or by means of a weighted lever. An apparatus of this kind, known as the Emerson Cotton Mill Power Scale, is illustrated in fig. 156, and its application to a spinning frame is shown in fig. 157. For these blocks we are indebted to the Florence Co., of Florence, Mass., who are the makers, and to whose pamphlet we must refer our readers for further particulars. The following results, which were obtained by applying one of these scales to a corn crusher, were kindly communicated to us by J. T. Potts :—

Material crushed.	Revs. per minute.	Lbs. ground per minute.	Horse-power required.
Oats,	161	8·3	0·874
Maize,	161	14·8	0·247
Beans,	161	17·7	0·410

when the crusher was moderately well lubricated, it required only 0·01 horse-power to drive it when doing no work; when allowed to go without oil for several days, the power was increased to 0·05 horse-power; whilst on thoroughly well oiling it the power required fell to 0·005 horse-power. It is evident that an appliance of this
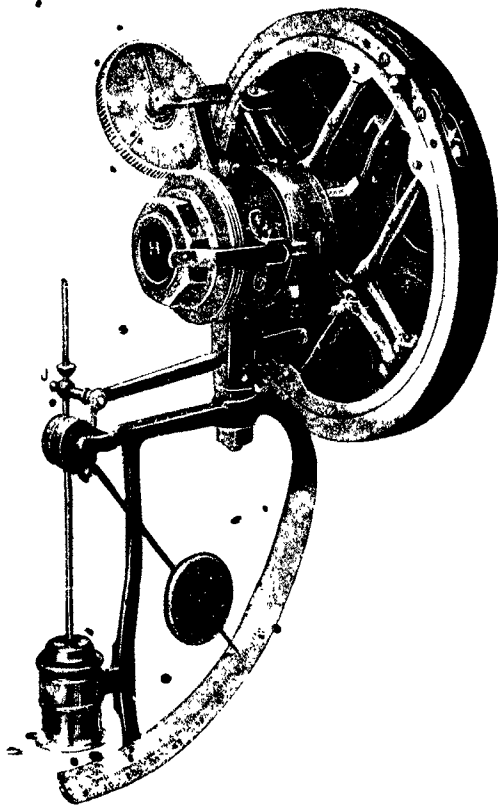
FIG. 156.

kind may prove very valuable in a large mill in determining the relative friction-reducing powers of various lubricants.

Frictional Losses.—*Magnitude of Losses.*—The losses which arise from the friction of the mechanism, as compared with the total energy actually expended in useful work, are in many cases unduly large. As an extreme case, a clock or watch may be instanced. Here, practically the whole of the power is expended in overcoming the

friction of the bearings, and the efficiency is zero. Should the friction of the pinions increase or diminish from any cause, then that of the speed-regulating appliance likewise diminishes or increases, the total friction remaining constant.

In a cotton mill, woollen factory, or printing works, the frictional losses are very large compared with the power actually developed. Here we have to deal with losses in the motor, the transmission machinery, and also in the actual machine tool, the power expended
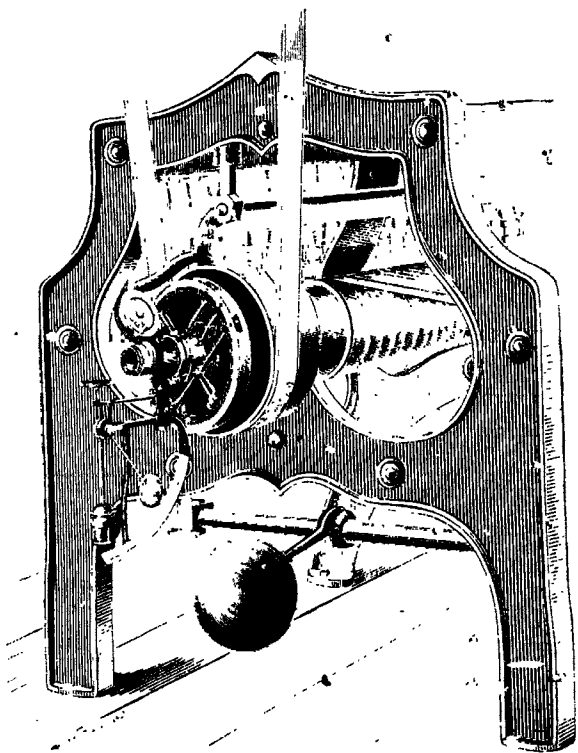
Fig. 157.

in placing the threads in position, or propelling the paper, ink, rollers, etc., being small. In electric-light and hydraulic stations, the efficiency of the installation is greater, for the total power delivered in the form of current or volume of water raised, is large in comparison with that developed by the motors.

Ordinary atmospheric changes of temperature have at times been

known to alter the friction of the machinery of a large mill as much as 15 or 20 per cent. In other instances, a reduction of 50 per cent. in the total resistance, and, therefore, of the fuel, etc., used, has been effected by using a more suitable oil. When it is remembered that this means that the frictional loss sometimes amounts to considerably more than half the power developed by the motor, the importance of using a suitable lubricant will be fully appreciated.

As the viscosity decreases, sometimes rapidly, with rise of temperature, a lubricant which may be suitable for one season or country may not suit another. The effects brought about in this way may be seen by comparing the coal burned from week to week during the year with the changes the mean temperature has undergone during the same intervals. In railway work this is particularly noticeable, the coal consumption, partly on this account, being much greater during winter months than in the summer.

Even after a mill has stood for a day, the bearings will have cooled down so much that considerably more power will be required to work it during the first few hours than during the rest of the run, providing the temperature of the air does not fall much in the interval. This must be borne in mind when, for the purpose of ascertaining the efficiency of any particular lubricant, the indicated horse-power required to drive a mill is measured.

The Efficiency of Mechanism.—In a machine shop or factory where power is used for carrying on any process, we generally have a *prime mover* which renders available the energy derived from some natural source, and *transmission machinery* for conveying the power so obtained to any point for the actuation of *special machinery* or *machine tools*. The mechanical efficiency of the motor or of any link in the mechanism involved in the transmission of power is obtained by dividing the useful work performed by the gross energy expended. Thus, in the case of a steam engine, if the indicated horse-power be 100, and the work actually delivered on the belt be 85, the efficiency would be 0·85.

In some cases the losses arising from the friction of shafting, etc., are so great that it is more economical to transmit the power electrically from the prime mover to the machine, which is then fitted with a small electro-motor.

Electrical Transmission of Power.—The use of electrical methods for the transmission of energy is now engaging the serious attention of mechanical engineers, for it enables the frictional losses of bearings to be, to a large extent, avoided. The resistance of the electrical conductors, however, also results in considerable loss of energy, and their capital cost being also large, electrical methods of transmission are not always the most economical; but where power has to be transmitted to a number of scattered points, it is often best to have a well-designed central generating station, and to transmit the energy electrically to the several shops or yards.

Economical Lubrication.—Before one can establish the fact that a

particular oil is more economical in use than another, a balance-sheet must be drawn up showing the total expenses chargeable to each of the following items :—

1. Cost of power developed.

2. Cost of proportion of power lost in friction.

3. Expenses resulting from wear and tear.

4. Cost of lubricants.

When the lubricants are very unsuitable, the bearings improperly designed, or there is careless management, other losses may be incurred which will not fall under either of the above heads. They include broken shafts, heated bearings, rapid wear, etc. It is such signs that often first direct attention to the fact that the lubricants in use are unsuitable. Even when such accidents are comparatively rare, the loss by friction may be much greater than it ought to be, and the fact that comparatively little difficulty is experienced in keeping the bearings from actually getting hot should not be regarded as showing that good results are being obtained as regards economy of power.

Indicating of Motors. When once the necessary gear has been fitted for indicating an engine, the difficulty of ascertaining the horse-power at any given moment is very small. Apart from the question of friction, a large motor should have indicator diagrams taken periodically for the purpose of ascertaining whether the valves are properly set and the distribution of steam satisfactory. For the best method of procedure, a work on the indicator should be consulted. We may here point out, however, that fluctuations in speed and power are produced by the action of the governors, etc, from minute to minute, and that accurate figures can only be obtained by making a series of observations extending over a reasonable interval of time, the mean of the results obtained from each set of indicator cards being made use of.

Estimation of Cost of Frictional Losses.-- As in many cases almost the whole of the losses are due to the friction of lubricated bearings, the losses due to each portion of the mechanism should, as far as possible, be ascertained separately. This may be done by obtaining the indicated horse-power under the following conditions :-

(*a*) Motor running light.

(*b*) With the transmission machinery in motion.

(*c*) With all the machines, or certain types of machines, running light.

(*d*) With all the machines, or certain types of machines, having their full working load on.

As the viscosity of lubricants varies with the temperature, the tests to ascertain the comparative lubricating values of two oils, etc., should be made under similar atmospheric conditions, and it is of equal, if not of greater, importance to give the bearings time to assume a steady temperature by indicating the motor at the end of a few hours' run.

To obtain the actual cost per hour per horse-power developed in ordinary running, the calculation should include the following items:—

1. Interest on cost of land, plant and buildings.
2. Depreciation (maintenance and renewal).
3. Taxes, insurance, etc.
4. Wages and salaries.
5. Cost of fuel, oil, waste, etc.

Here we have a number of charges which increase or decrease the cost of power according as the mean output decreases or increases. It may be argued that the saving effected by improving the lubrication, inasmuch as it does not decrease some of these items, should be calculated upon the saving in item 5 only. However, when the saving in power is large, it may affect depreciation and wages as well. This is a point the consideration of which must be left to the judgment of the engineer in charge.

It has been shown that the friction of a steam-engine or gas-engine is unaffected by the load put upon it. Thus if, when running light, the indicated horse-power is 7, then, when the brake horse-power is 50, the indicated horse-power will be 57. From this it is clear that the frictional resistance, measured when there is no load on the engine, gives the frictional resistance under all conditions. The same will apply to line shafting and to many machines and machine tools. We may, therefore, estimate very closely the friction-reducing properties of any particular lubricant by running the machinery oiled with it light, rather than fully loaded ; care must, however, be taken always to have the same number of machines at work when making a test.

When the horse-power developed by the motor is large, and the machines numerous, the effect of changing an oil can only be ascertained by using it on a large number of bearings or machines, so as to make the loss or gain of power considerable in proportion to the total effect.

By multiplying the gain or loss of power by the cost per horse-power, and then by the hours worked per diem, the daily saving or loss is obtained, and by comparing this with the oil account the real commercial value of the lubricant is ascertained. The point has been dealt with at some length by R. H. Thurston.[1]

Since the increase in friction of a bearing results in a rise of the temperature of the pedestal, a rough idea of the comparative value of two lubricants may be obtained by measuring their temperature effects. This is most satisfactorily effected by surrounding two bearings on a shaft by roomy boxes, to protect them from draughts, and placing thermometers in contact with the pedestal caps. The same oil should first be tried on both bearings, and the rise of temperature of each noted, for with the same oil different bearings will almost always be found to give somewhat different heating results. When the difference of temperature which results from the accidental

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[1] *Friction and Lost Work*, p. 343.

difference of load or condition of each bearing has been ascertained, the oil used for one of them may be changed and a comparative test again made. This should be done several times, for the result depends in some measure upon the rate of feed.

It is, however, much more satisfactory to make such ci-tests in proper oil-testing machines, for the load, speed, and the rate of and method of feed can then be properly controlled.

Estimation of Losses due to Wear.—These can only be obtained in a direct way by comparing the expense incurred in repairs, renewals, and breakdowns which have occurred during fairly long intervals of time. However, it is sometimes necessary to obtain the effects produced during short intervals by different lubricants, in which case the best plan is to weigh certain brasses o. other rubbing parts, such as piston rings, at stated intervals on an accurate balance. In this way any rapid increase or decrease in the rate of wear can be noted, and this, taken in connection with the pecuniary gain or loss resulting from a variation in the total frictional losses, will enable the engineer to form a fairly accurate estimate of the value, from a practical point of view, of the particular lubricant.

In all cases where frictional losses form a large proportion of the power developed, it will be found that the cost of the lubricant, being only about 3 per cent. of the cost of fuel, is a comparatively insignificant item compared with that of the power saved or lost. Indeed, it will frequently pay to use the best lubricant irrespective of its price. The highest-priced lubricant offered, however, is often by no means the best, for very poor mixtures are sometimes placed upon the market as first-class lubricants and sold at high prices.

Oil cans, Feeders, etc.—Vessels for holding a supply of oil and enabling it to be supplied to the bearings with ease and certainty are made of various patterns. In some cases it is only necessary to supply a few drops once every few hours. For this purpose small conical or lenticular cans, having a long spout screwed on, are convenient. Either the bottom or sides are made elastic, and a little pressure exerted compresses them and expels a small quantity of oil. In the larger forms the oil is liberated by opening a small valve actuated by a button, or the piston of a small cylinder is pressed in and any desired amount of oil delivered.

It sometimes happens that the reservoirs of oil-bath bearings have to be emptied and filled again periodically. For this purpose a form of syringe is used which enables a definite quantity to be withdrawn from the bottom of the reservoir and fresh oil substituted.

INDEX.